An extended salt-effect model for organic solubility of water in a 5-100% tri-\textit{n}\-butyl phosphate/diluent/nitric acid/water biphasic system at 298.15 K

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Received 2 January 2007; revised 11 February 2008

The solubility of water in the organic solutions, containing hydrocarbons, has traditionally been modeled by using empirical correlations. In this communication, an extended Setschenow model is proposed for predicting the organic solubility of water in a 5-100% tri-\textit{n}\-butyl phosphate/diluent-nitric acid-water biphasic system at 298.2 K. The literature data on water solubility were correlated to aqueous acid concentration and diluent concentration in the solvents. The proposed model was extended for temperature dependency of the solubility.

Keywords: Solubility, PUREX process, TBP, Salt-effect, Setschenow models

The solubility of water in the organic solutions, containing hydrocarbons, has traditionally been modeled by using empirical correlations. Tri-\textit{n}\-butyl phosphate (TBP) is the extractant employed in the PUREX (Plutonium Uranium Extraction) process for separating uranium and plutonium from spent nuclear fuel. In the PUREX process, the usual TBP concentration is 30% on volume basis. In the Interim-23 process, for the separation of U-233 from irradiated thorium, 5% TBP is used as solvent. The conventional PUREX solvent components (TBP and hydrocarbon diluent) are unique\textsuperscript{1} in the sense that water is appreciably soluble in the TBP to the tune of 3.59 mol/L whereas water solubility in the \textit{n}\-dodecane\textsuperscript{2} diluent is limited to $\sim$2.7$\times$10$^{-5}$ mol/L. The amount of water extracted into the organic phase (along with the other extracting solutes like nitric acid, UO$_2$(NO$_3$)$_2$ and Pu(NO$_3$)$_4$) causes appreciable phase volume changes. In the computer simulation codes (SEPHIS\textsuperscript{3} and SIMPSEX\textsuperscript{4}) for the PUREX process, it is handled empirically. For proper understanding of the phase volume change due to water extraction and related behaviour, a mechanistic model is desired.

Salt-effect model

Aqueous solubility of a non-electrolyte in the presence of an electrolyte salt was studied empirically by Setschenow\textsuperscript{5}. He observed that the solubility could be correlated by the following empirical relation:

$$\log_{10}\left(\frac{S_{ne}^0}{S_{ne}}\right) = k \ C_E$$

where $S_{ne}^0$ and $S_{ne}$ are the aqueous solubilities of non-electrolyte in the absence of the salt and in the presence of the salt respectively, $k$ is the salting coefficient, now named after Setschenow and $C_E$ is the concentration of the electrolyte salt. The relationship, shown in Eq. (1), 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 McDevit\textsuperscript{6} and Gordon\textsuperscript{7}.

There are no comprehensive models available in the open literature for prediction of the organic solubility of water in the PUREX solvent with varying concentration of the diluent and to account for the interaction between the electrolyte solute and TBP.

Discussion

Gordon\textsuperscript{7} mentioned that the molal activity coefficient ($\gamma_S$) of a non-electrolyte S, in the presence of an 1:1 electrolyte E (On dissociation, it will yield one univalent cation and one univalent anion) could be represented as power series in $m_E$ and $m_S$

$$\log \gamma_S = \sum_{i=1}^{\infty} K_im_i^E + \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} b_{ij}m_i^em_j^E$$
where $K_i$ are the Setschenow coefficients; $b_{ij}$ is interaction parameter and $m_E$ and $m_S$ are molal concentrations of electrolyte E and non-electrolyte S respectively, $\gamma$ is activity coefficient and $i$, $j$ are counters. Gordon also mentioned that the effect of presence of other non-electrolytes on the activity coefficient of the non-electrolyte could be correlated in the form of a power series. The use of the molal scale of concentration is not very convenient, therefore, at high solute concentrations, the conventional form of the Setschenow equation is expressed in terms of molar concentrations. Thus Eq. (2) is rewritten as power series in $C_S$ and $C_E$,

$$\log \gamma_S = \sum_{i=1}^{\infty} k_i C^i_E + \sum_{i=0}^{\infty} b_{ij} C^i_S C^j_E$$

... (3)

where $\gamma_S$ is the activity coefficient of the non-electrolyte S on the molar scale and $C_E$ and $C_S$ are molar concentrations of electrolyte E and non-electrolyte S respectively. Alcock et al. defines the ratio of solubilities $S^0/S$ as the activity coefficient on the molar scale ($\gamma_s$) whereas from theoretical considerations, it should be taken as ($\gamma_s/\gamma_s^o$).

It has been observed that the reported data on organic solubility of water in the 5, 10, 15, 30, 65 and 100% TBP could be predicted well with a sufficient accuracy by the following extended Setschenow equation,

$$\log \left(\frac{S^0}{S}\right) = \sum_{i=1}^{\infty} A_i C^i_{\text{Dil}} + \sum_{i=1}^{\infty} k_i C^i_{\text{HNO}_3} + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} b_{ij} C^i_{\text{HNO}_3} C^j_{\text{Dil}}$$

... (4)

where $A_i$ terms are adjustable parameters, $C_{\text{Dil}}$ is the molar concentration of diluent in the organic solvent, $S^0$ is the solubility of water into pure TBP at 298.15 K at zero aqueous acidity. Eq. (4) has essentially the same form as Eq. (3) with a limited number of terms. As nitric acid concentration ranged between 0–8 kmol/m³, higher order terms were added to the basic Setschenow equation. As diluent concentration also varied from 0 to 100%, higher order coefficients were required in the diluent term in the Eq. (4). Least-square determined constants of Eq. (4) are listed in Table 1. Eq. (4) is essentially an extended form of the basic Setschenow equation. The deviations were calculated as 100*(measured-experimental)/experimental. The average deviation and the standard deviation for 104 experimental points were 1.50 and 11.06% respectively. Figure 1 is a Setschenow plot. It shows that the slope of aqueous acidity versus $\log(S^0/S)$ varies with acidity in a highly non-linear fashion, thus the use of higher order terms in Eq. (4) is justified. Figure 2 is a parity plot. Figure 3 is a plot of comparisons between the experimental and the predicted solubility for various aqueous acidities and organic TBP concentrations. It shows variation of organic solubility of water with varying aqueous acidity and varying TBP concentration in the organic phase. Figure 4 is a similar plot at zero aqueous acidity. A good agreement between reported experimental data and predicted values was observed. Details of the database have been listed in Table 2. The analysis reported in this work is limited to the n-dodecane or similar diluents (C12 Alkane as a major constituent).
Table 2—Details of the database

<table>
<thead>
<tr>
<th>S.No</th>
<th>Reference</th>
<th>TBP Conc.</th>
<th>Vol.%</th>
<th>Diluent</th>
<th>No. of points</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Davis (1962)</td>
<td>5-100</td>
<td></td>
<td>Amsco 125-82*</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>Johnson and Dillon (1953)</td>
<td>2.5-70</td>
<td></td>
<td>n-Dodecane*</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>Burger and Forsmann (1951)</td>
<td>5-100</td>
<td></td>
<td>Amsco 125-90 W</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>Wagner and Farrand (1960)</td>
<td>5-70</td>
<td></td>
<td>Amsco 125-82*</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>Burger (1984)</td>
<td>100</td>
<td></td>
<td>Nil</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Total no. of points</td>
<td></td>
<td></td>
<td></td>
<td>104</td>
</tr>
</tbody>
</table>

*In calculations, only n-dodecane parameters were used. i.e., \( C_{\text{Dil}} = C_{\text{add}} = (1 - F) \times 1000 \times \frac{\rho_{\text{add}}}{M_{\text{add}}} \), where \( F \) is the volume fraction of TBP in the solvent. Amsco series solvents are similar to n-dodecane and used in the past.

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Fig. 2—Parity plot for organic water concentrations in 5-100% TBP solvent at various aqueous acidities.

Fig. 3—Variation of experimental and predicted organic water concentrations in 5-100% TBP solvent at various aqueous acidities.

Fig. 4—Variation of experimental and predicted organic water concentrations in 5-100% TBP solvent at zero aqueous acidity.

In presence of \( N \) electrolyte solutes (extracted or not extracted by TBP), Eq. (4) may be extended as,

\[
\log \left( \frac{S^e}{S} \right) = \sum_{m=1}^{N_e} C_m^e + \sum_{i=1}^{N} \left( \sum_{j=1}^{N_e} k_{ij} C_j^i \right) + \sum_{i=1}^{N} \left( \sum_{j=1}^{N_e} \sum_{m=1}^{N} b_{ijk} C_m^i C_j^i \right) \quad \cdots (5)
\]

where \( C_k \) is the molar concentration of \( k \)th electrolyte. If a particular electrolytic solute is not extracted into the organic phase, its associated interaction parameter should be set to zero.

Temperature dependency of organic solubility of water in 100% TBP

Hardy et al.$^1$ had determined the solubility of water into 100% TBP at several temperatures in the range of 273.15 to 333.15 K. These values were normalized at 298.15 K and linear-regression was performed. The data could be correlated to the following empirical equation
$S^0(\text{T}) = S^0_{298.15} \left[ 1 - 3.9186 \times 10^{-4} (\text{\text{T} - 298.15}) - 7.3277 \times 10^{-6} (\text{\text{T} - 298.15})^2 \right] \quad \ldots (6)$

$S^0_{298.15}$ is the standard state value (3.59 kmol/m$^3$) of water in 100% TBP at zero aqueous acidity. Mean and standard deviations were 0.14 and 0.49%, respectively indicating a good agreement between reported experimental values and the predicted values.

Temperature dependency of organic solubility of water in TBP/diluent (mixed organic solution)

Now base solubility (standard state solubility) has been correlated for temperature dependence, following form of temperature dependency is assumed for the Setschenow coefficients

$$k(T) = k_{298.15} \left[ 1 + \alpha \left( \text{T} - 298.15 \right) + \beta \left( \text{T} - 298.15 \right)^2 \right] \quad \ldots (7)$$

On substituting respective equations for $S^0(\text{T})$ and $k(T)$, Eq. (5) may be written in the following form,

$$\log \left( \frac{S^0(\text{T})}{S} \right) = \sum_{i=1}^{N} \sum_{j=1}^{C} a_{ij} \left[ 1 + \alpha_i (\text{T} - 298.15) + \beta_i (\text{T} - 298.15)^2 \right] c_j^{\text{Dil}}$$

$$+ \sum_{i=1}^{N} \sum_{j=1}^{C} b_{ij} \left[ 1 + \alpha_i (\text{T} - 298.15) + \beta_i (\text{T} - 298.15)^2 \right] c_j^\text{TBP} c_j^\text{Dil} \quad \ldots (8)$$

where $\alpha_i$, $\alpha_{ij}$, $\alpha_{kij}$, $\beta_i$, $\beta_{ij}$ and $\beta_{kij}$, are temperature coefficients of the respective Setschenow coefficients. The constants of Eq. (8) could not be evaluated due to lack of experimental data at different temperatures.

Conclusions

Reported experimental data on organic solubility of water in 5-100% TBP/diluent (n-Dodecane or similar) nitric acid-water biphasic system at 298.2 K could be correlated satisfactorily by means of an extended Setschenow model. An extension is proposed for presence of multiple electrolytic solutes irrespective of the fact that they are extracted or not extracted by TBP. The form of the proposed model has been suggested to cover the temperature dependency of the organic solubility of water in the PUREX solvent.

Nomenclature

$A = \text{Empirical coefficients/adjustable parameters}$

$b = \text{Interaction parameter}$

$C = \text{Concentration on molar scale (mol/L or kmol/m}^3\text{)}$

$k$, $K = \text{Setschenow coefficients}$

$N = \text{Number of solutes}$

$\text{Dil} = \text{Diluent}$

$S = \text{Solubility (mol/L or kmol/m}^3\text{)}$

$S^0 = \text{Reference solubility (mol/L or kmol/m}^3\text{)}$

$T = \text{temperature (K)}$

$\text{TBP} = \text{Tri-n-butyl phosphate}$

$y_s = \text{Activity coefficient of non-electrolyte solute (molar scale)}$

$\gamma^0_s = \text{Activity coefficient of non-electrolyte solute (molar scale) at the standard state}$

Superscripts and subscripts

$i, j, k = \text{Counters}$

$0 = \text{Standard state value}$

Greek symbols

$\gamma_s = \text{Molal activity coefficient of non-electrolyte solute}$

$\alpha, \beta = \text{Temperature coefficients of the respective Setschenow coefficients}$

References


