Modelling of distribution coefficients of nitrous acid in 15-30 vol.% TBP/n-dodecane–nitric acid system

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Received 29 June 1999; accepted 22 September 2000

During partitioning of uranium and plutonium, nitrous acid re-oxidises Pu(III) to Pu(IV). Therefore a large excess of U(IV) is required. Since the scavenger reagent “hydrazine” is not extracted into the organic phase, even a small amount of extracted nitrous acid will cause cyclic reactions in the organic phase. In this scenario, study of the distribution behaviour of nitrous acid is important. In this paper, a model, based on extraction mechanism, is reported and compared with the model reported in the literature. The model reported here is considered more reliable than the model available in the literature.

In the contemporary salt-free reprocessing flowsheets, it is quite common to use U(IV) as a reductant for partitioning of uranium and plutonium. In a U(IV) based partitioning system, chemical reactions that take place are

\[
\begin{align}
U^{4+} + NO_3^- + H_2O &\rightleftharpoons UO_2^{2+} + HNO_2 + H^+ & \quad \text{(1)} \\
2Pu^{3+} + NO_3^- + 3H^+ &\rightleftharpoons 2Pu^{4+} + HNO_2 + H_2O & \quad \text{(2)} \\
U^{4+} + 2HNO_2 &\rightarrow UO_2^{2+} + 2H^+ + 2NO \uparrow & \quad \text{(3)} \\
Pu^{3+} + HNO_2 + H^+ &\rightarrow Pu^{4+} + H_2O + NO \uparrow & \quad \text{(4)} \\
2NO + HNO_3 &\rightarrow 2HNO_2 & \quad \text{(5)}
\end{align}
\]

As shown above, nitrous acid re-oxidises Pu(III) to Pu(IV). Therefore a large excess of U(IV) is required. To stabilize U(IV), hydrazine is added to the partitioning system. Hydrazine work as scavenger for nitrous acid. As hydrazine is not extracted into the organic phase, even a small amount of extracted nitrous acid will cause cyclic reactions in the organic phase\(^3\). In this scenario, study of the distribution behaviour of nitrous acid is important.

Fletcher et al.\(^7\) reported that the solvation number for complex of nitrous acid and TBP could be assumed as unity. Therefore extraction mechanism may be written as

\[
H^+ + NO_2^- + TBP_f \rightleftharpoons HNO_2.TBP & \quad \text{(6)}
\]

Pseudo-equilibrium can be assumed and a pseudo-equilibrium parameter may be obtained as

\[
k = \frac{(HNO_2.TBP)}{\sum H^+(TBP_f)\left[NO_2^\right]} \quad \text{(7)}
\]

If aqueous concentration of nitrous acid is small and there is no other source of nitrite ion present then distribution coefficient for nitrous acid could be written as

\[
K_d = \frac{(HNO_2.TBP)}{\left[NO_2^\right]} \quad \text{(8)}
\]

On substituting Eq. (8) in the Eq. (7), one gets-

\[
K_d = k * TBP_f \left(\sum H^+\right) \quad \text{(9)}
\]

Now the pseudo-equilibrium parameter \(k\) may be correlated with the system properties. However it was observed by some authors that the product of \(k\) and the acidity (or total nitrate salting strength) correlated better than that \(k\) alone.

Discussion

Earlier work

Bernard \textit{et al.}\(^3\) reported the following correlation with different values of parameter \(K\) for 15%, 20% and 30% TBP/n-dodecane systems.

\[
K_d = K * TBP_f \quad \text{(10)}
\]

The parameter \(K\) is analogous to the product of \(k\) and the total aqueous acidity. Numerical values of \(K\) were reported \(^3\) to be 17.2, 18.5 and 18.0 for 15%, 20% and 30% TBP/n-dodecane systems respectively. Authors compiled a database from literature\(^3\) and
tested equation of Bernard et al.\textsuperscript{3} with it. For a set of 49 experimental points for TBP concentration of 15%, 20% and 30% and \( K \) values listed above, standard deviation was 14.6%.

**Present work**

Authors observed that the parameter \( K \) of Eq. (10) could be correlated with TBP concentration in the organic phase, total acidity of the aqueous phase and the total nitrate salting strength of the aqueous phase with a sufficient accuracy. Correlated equation was:

\[
K = 10.9978 \times F^{0.1296} \times (L:H^{+})^{-0.4347} \times \exp(0.2632 \times (L:NO_{3}^{-}))
\]  

(11)

Predicted values of \( K \) from Eq. (11) were used in predicting distribution coefficient from Eq. (10) and for the same set of 49 experimental points, the standard deviation was 11.3%. This value is smaller than that for Eq. (10) with the \( K \) values of Bernard et al.\textsuperscript{3}. Fig. 1 shows a parity plot for distribution coefficients of nitrous acid. Fig. 2 shows a plot of residuals (Predicted-experimental). Agreement between predicted and experimental values is quite good. All the calculations were done in MATLAB 5.0 in Windows-98 OS on a contemporary P-II computer.

The above reported model for nitrous acid distribution coefficients is being integrated with indigenously developed purex simulation code SIMPSEX and it is expected that use of this model would improve accuracy for simulation of partitioning operation.

**Conclusion**

In this paper, reported data on nitrous acid distribution in 15-30\% TBP/n-dodecane-water-nitric acid system is analysed. A model, based on extraction mechanism, is reported and compared with the model reported in the literature. The model reported here is considered more reliable than the model available in the literature.

**Nomenclature**

\( F \) = volume fraction of TBP in the organic solvent  
\( k \) = pseudo-equilibrium parameter  
\( K \) = pseudo-equilibrium parameter \((k \times \Sigma (NO_{3}^{-}))\)  
\( K_{d} \) = distribution coefficient  
\( Pu \) = plutonium  
\( TBP \) = tri-n-Butyl Phosphate  
\( TBP_{f} \) = free TBP concentration (mol/L)  
\( U \) = uranium  
\( \Sigma H^{+} \) = total hydrogen ion strength from acids (mol/L)  
\( \Sigma NO_{3}^{-} \) = total nitrate salting strength in the aqueous phase (mol/L)

**References**