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The SX Solver: A Computer Program for Analyzing Solvent-Extraction Equilibria: Version 3.0

G. J. Lumetta

January 2002



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Summary

A new computer program, the SX Solver, has been developed to analyze solvent-extraction equilibria. The program operates out of Microsoft Excel® and uses the built-in "Solver" function to minimize the sum of the square of the residuals between measured and calculated distribution coefficients. The extraction of nitric acid by tributyl phosphate has been modeled to illustrate the program's use.

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Introduction

Equilibria phenomena are of central importance to solvent-extraction science. Such phenomena have been investigated for many decades. Two primary methods are employed in studying solvent-extraction equilibria—graphical methods (slope analysis) and numerical methods (computer modeling). Despite the widespread availability of computers, graphical methods are still extensively used. A few years ago, we introduced a Visual Basic Application for Microsoft Excel® designed for analyzing solvent-extraction equilibria (Lumetta et al. 1999). This program was named the *SX Solver*. The SX Solver program takes advantage of the graphical user-interface of Excel®, so it is designed to be user-friendly. However, the initial version of the SX Solver had several limitations. The program has been upgraded to overcome many of these. The latest version contains the following enhancements:

- Activity coefficients for mixed electrolyte systems can be calculated.
- The coextraction of acid with the metal ion can be included in the model.
- Aqueous-phase metal complexation can be incorporated into the model.

In addition, minor enhancements to the user interface have been introduced.

Model Description

The SX Solver model is based on the following general equation for the extraction of a metal cation (M^{z^+}) by a neutral ligand (L):

$$mM^{z^{+}}(aq) + qH^{+}(aq) + xX^{y^{-}}(aq) + pL(org) \Leftrightarrow M_{m}H_{q}X_{x}L_{p}(org)$$
(1)

where x = (mz+q)/y. The equilibrium constant for this reaction is defined as^(a)

$$K = \frac{y_{C}[M_{m}H_{q}X_{x}L_{p}]_{o}}{(y_{M}[M]_{a})^{m}(y_{H}[H]_{a})^{q}(y_{X}[X]_{a})^{x}(y_{L}[L]_{o})^{p}}$$
(2)

where y_C , y_M , y_H , y_X , and y_L are the molar-scale activity coefficients for $M_m X_{(mz/y)} L_p$, M^{z^+} , H^+ , X^{y^-} , and L, respectively. Quantities in brackets refer to the molar concentration of the individual species. The subscripts "a" and "o" refer to species in the aqueous and organic phases, respectively. This expression can be rearranged to yield an expression for the concentration of the extracted specie.

$$[M_{m}H_{q}X_{x}L_{p}]_{o} = \frac{y_{M}^{m}y_{H}^{q}y_{X}^{x}y_{L}^{p}}{y_{C}} \bullet K[M]_{a}^{m}[H]_{a}^{q}[X]_{a}^{x}[L]_{o}^{p}$$
(3)

The distribution coefficient is defined as the total concentration of the metal in the organic phase divided by the total concentration in the aqueous phase, and is given by the following equation:

$$D = \frac{[M]_{o}}{[M]_{a}} = \frac{m[M_{m}H_{q}X_{x}L_{p}]_{o}}{[M]_{a}}$$
(4)

It should be noted that $[M]_a$ represents the total metal concentration in aqueous phase. To determine the concentration of the free metal ion, $[M^{z^+}]$, the complexation of M^{z^+} by X^{y^-} in the aqueous phase must be taken into account. The complexation of M^{z^+} by X^{y^-} can be accounted for in terms of the individual formation constants:

$$M + X \leftrightarrow MX ; B_1 = \frac{[MX]}{[M][X]} \text{ or } [MX] = B_1[M][X]$$
$$M + 2X \leftrightarrow MX_2 ; B_2 = \frac{[MX_2]}{[M][X]^2} \text{ or } [MX_2] = B_2[M][X]^2$$

etc.

$$M + nX \leftrightarrow MX_{n} ; B_{n} = \frac{[MX_{n}]}{[M][X]^{n}} \text{ or } [MX_{n}] = B_{n}[M][X]^{n}$$
(5)

⁽a) In the following equations, the ionic charges are omitted for clarity.

The total metal concentration in the aqueous phase is given by:

$$[M]_{a} = [M] + [MX] + [MX_{2}] + \dots [MX_{n}]$$
(6)

Combining Equations (5) and (6) yields the expression for the total aqueous-phase metal concentration:

$$[M]_{a} = [M] + \sum_{t=1}^{n} B_{t}[M][X]^{t}$$
(7)

So, for the case when a single specie $(M_mH_qX_xL_p)$ is formed during the extraction, the expression for the distribution coefficient can be obtained by combining Equations 3, 4, and 7.

$$D = \frac{\frac{y_{M}^{m} y_{H}^{q} y_{X}^{x} y_{L}^{p}}{y_{C}} \bullet mK[M]_{a}^{m}[H]_{a}^{q}[X]_{a}^{x}[L]_{o}^{p}}{[M] + \sum_{t=1}^{n} B_{t}[M][X]^{t}}$$
(8)

If more than one extraction equilibrium (of the type shown in Eq. 1) is involved, the total organicphase metal concentration is given by:

$$[\mathbf{M}]_{o} = \sum_{i} m_{i} [\mathbf{M}_{m_{i}} \mathbf{H}_{q_{i}} \mathbf{X}_{x_{i}} \mathbf{L}_{p_{i}}]_{o}$$
(9)

and Equation 8 becomes

$$D = \frac{\sum_{i} \frac{y_{M}^{m_{i}} y_{H}^{q_{i}} y_{X}^{x_{i}} y_{L}^{p_{i}}}{y_{C_{i}}} \bullet m_{i} K_{i} [M]^{m_{i}} [H]_{a}^{q_{i}} [X]_{a}^{x_{i}} [L]_{o}^{p_{i}}}{[M] + \sum_{t=0}^{n} B_{t} [M] [X]^{t}}$$
(10)

where K_i is the extraction constant for specie i.

Program Description

Equation (10) is general for extraction of metal ions by a neutral extractant, provided the extracted species are not ionic in nature (as might occur in highly polar solvents). Distribution data can be fit to this equation using nonlinear regression techniques. The SX Solver is a spreadsheet application that uses the Microsoft Excel® "Solver" function to minimize the function:

$$SSR = \sum w(D - D_{calcd})^2$$
(11)

where D and D_{calcd} are the measured and calculated distribution coefficients, respectively, for a given measurement, and w is a weighting factor defined by the user. D_{calcd} is determined through Equation 10.

Calculating the D values through Equation 10 requires knowledge of $[M^{z^+}]_a$, $[H^+]_a$, $[L]_o$, and $[X^{y^-}]_a$. To determine these concentrations, it is necessary to solve the mass-balance equations for the metal, acid (H), the anion, and the extractant; these mass-balance equations are given in Equations 12, 13, 14, and 15, respectively.

$$\left[\left(\frac{V_o}{V_a} \right) \sum_i \frac{y_M^{m_i} y_H^{q_i} y_X^{x_i} y_L^{p_i}}{y_{C_i}} \bullet m_i K_i [M]^{m_i} [H]^{q_i} [X]^{x_i} [L]^{p_i} \right] + [M] - [M]_{tot} + \sum_{l=0}^n B_l [M] [X]^l = 0$$
(12)

$$\left[\left(\frac{V_{o}}{V_{a}} \right) \sum_{j} \frac{y_{H}^{a_{j}} y_{X}^{a_{j}/y} y_{L}^{b_{j}}}{y_{HC_{j}}} \bullet a_{j} K_{H_{j}} [H]^{a_{j}} [X]^{a_{j}/y} [L]^{b_{j}} \right] + \left[\left(\frac{V_{o}}{V_{a}} \right) \sum_{i} \frac{y_{M}^{m_{i}} y_{H}^{q_{i}} y_{X}^{x_{j}} y_{L}^{p_{i}}}{y_{C_{i}}} \bullet q_{i} K_{i} [M]^{m_{i}} [H]^{q_{i}} [X]^{x_{i}} [L]^{p_{i}} \right]$$
$$+ [H] - [H]_{tot} = 0$$
(13)

The terms a_j and b_j in the above equations are derived from the extraction of H_yX into the organic phase by association with L according to the following equation.

$$aH^{+}(aq) + (a/y)X^{y}(aq) + bL(org) \Leftrightarrow H_{a}X_{(a/y)}L_{b}(org)$$
(16)

As was the case with the extraction of M^{z+} , a number of extracted acid species can be considered (the various species being represented by the term "j" in Equations 13 through 15. The term y_{HC} is the activity coefficient for $H_a X_{(a/y)} L_b$.

$$\left[\left(\frac{V_o}{V_a} \right) \sum_j \frac{y_H^{a_j y} y_X^{a_j y} y_L^{b_j}}{y_{HC_j}} \bullet b_j K_{H_j} [H]^{a_j} [X]^{a_j y} [L]^{b_j} \right] + \left[\left(\frac{V_o}{V_a} \right) \sum_i \frac{y_M^{m_i} y_H^{q_i} y_X^{x_i} y_L^{p_i}}{y_{C_i}} \bullet p_i K_i [M]^{m_i} [H]^{q_i} [X]^{x_i} [L]^{p_i} \right]$$

$$+ [L] - [L]_{tot} = 0$$
(14)

In the SX Solver program, the aqueous-phase activity coefficients are determined using the method established by Bromley (1973), which was described in detail by Vandegrift et al. (1990) for multicomponent electrolyte solutions. For this calculation, molar concentrations are converted to molal concentrations using a second-order polynomial fit to plots of molality versus molarity. The Bromley method yields the molal-scale activity coefficient, which is converted to the molar-scale activity coefficient by applying the formula (Robinson and Stokes 1959): $y_{\pm} = \gamma_{\pm} m d_o/c$, where γ_{\pm} is the molal-scale activity coefficient, m is the molal concentration, c is the molar concentration, and d_o is the density of water (0.9971 g/mL at 25°C). Currently, the program only supports activity calculations for nitrate solutions containing Am³⁺, Cd²⁺, Eu³⁺, H⁺, Na⁺, Nd³⁺, UO₂²⁺, Th⁴⁺, and/or Li⁺.

$$\left[\left(\frac{V_{o}}{V_{a}} \right) \sum_{j} \frac{y_{H}^{a_{j}} y_{X}^{a_{j}/y} y_{L}^{b_{j}}}{y_{HC_{j}}} \bullet \frac{a_{j}}{y} K_{H_{j}} [H]^{a_{j}} [X]^{a_{j}/y} [L]^{b_{j}} \right] + \left[\left(\frac{V_{o}}{V_{a}} \right) \sum_{i} \frac{y_{M}^{m_{i}} y_{H}^{q_{i}} y_{X}^{s_{i}} y_{L}^{p_{i}}}{y_{C_{i}}} \bullet x_{i} K_{i} [M]^{m_{i}} [H]^{q_{i}} [X]^{x_{i}} [L]^{p_{i}} \right]$$

+[X]-[X]_{tot} +
$$\sum_{l=0}^{n} lB_{l}[M][X]^{l} = 0$$
 (15)

It is assumed that all of the extractant remains in the organic phase. The activity coefficient for the extractant L in the organic phase is estimated by the Hildebrand-Scott model (Hildebrand and Scott 1950), which has been successfully employed in the SXLSQA program (Baes et al. 1990). A description of the procedure used to calculate the ligand-activity coefficients can be found in Baes et al. (1990). It should be noted that the SX Solver program allows the user to assume ideality in either the organic or aqueous phases, in which case, the activity coefficients are set to unity. The activity coefficients for the extracted species (yC) are assumed to be one.

The SX Solver program uses an iterative procedure to solve the set of simultaneous equations consisting of Equations 12 through 15. Figure 1 describes this iterative approach. In essence, values for [M]tot, [H]tot, [L]tot, [X]tot, and the extraction constants are input into the procedure. Then values are calculated for [M]a, [H]a, [L]o, and [X]a using Newton's method of approximation to solve Equations 12 through 15, respectively. This is achieved by applying Equation 17:

$$\mathbf{C} = \mathbf{C}^* - \frac{\mathbf{f}(\mathbf{C}^*)}{\mathbf{f}(\mathbf{C}^*)} \tag{17}$$

where C represents the concentration being determined (i.e., $[M]_a$, $[H]_a$, $[X]_a$, and $[L]_o$). A reasonable initial value is chosen for C (in this case, C_{tot} is used as the initial value), and this is assigned as the value of C^{*}. The function, $f(C^*)$, is then calculated according to Equations 12, 13, 14, or 15; the function $f'(C^*)$ is the derivative of Equations 12, 13, 14, or 15 with respect to C. A new value for C is obtained by applying Equation 17. This new value is assigned as C^{*}, and the process is repeated until there is no significant change between C and C^{*}.



Figure 1. Iterative Scheme Used To Solve Equations 12 Through 15. After each iteration, the change in the value represented by the sum of Equations 12 through 15 (which in theory should be zero when a solution is obtained) from the previous iteration is compared to a target value (0.00001).

Program Operation

Copying Program Files

The SX Solver application consists of two Excel® files—*SXSolver3.0.xls* and *MixedElectrolyteCalc.xls*. These two files must be copied to the same folder (or directory). It is recommended that a folder titled "SXSolver" be established on the computer hard drive.^(a) This would typically have the address X:/SXSolver, where X is the letter designating the hard drive. The files SXSolver3.0.xls and MixedElectrolyteCalc.xls should be copied to this folder.

Starting the Program

To start the SX Solver program, start MS Excel®. From the menu bar, choose "File" then "Open." This brings up the Open Files dialog box. Use the "Look in" pull-down menu to navigate to the SXSolver folder. Choose the file SXSolver3.0.xls and click the "Open" button. A message box will appear, indicating that the file contains macros. Click the "Enable Macros" button. The SX Solver "Launch Sheet" will then appear.

Launch Sheet Description

The Launch Sheet contains four buttons. These are described in Table 1, along with their function.

Button ID	Button Description	Function
1	Is this a new experiment?	Clicking this button will clear all previous data
1	If so, click here to clear previous data.	and reset the SX Solver application
2	To enter your solvent extraction data	Takes the user to the data-entry sheet
2	Click Here	
	If you want to skip the data entry step	Allows the user to skip the data-entry step. This
3	Click Here	can be used when the user wants to resume
		modeling data that were previously entered.
	Hey, if you only want to calculate the	This feature allows calculation of the activity
4	activity coefficients for a	coefficients and density of a multicomponent
4	multicomponent electrolyte solution,	electrolyte solution without running the full SX
	Click Here	Solver program.

Table 1. Description and Function of Launch Sheet Buttons

When first using the SX Solver or when beginning to model a new set of extraction data, it is essential to click Button 1. This will reset the application. Logically, the next step is to enter the extraction data. Clicking Button 2 will take the user to the data-entry sheet, which is discussed below. Often it is desirable to skip the data-entry step. This is typically the case if the user was interrupted in the

⁽a) The user can choose any folder name. However, in this report, it is assumed that the folder name is "SXSolver."

processing of a given data set. Pressing Button 3 allows the user to run the SX Solver application without having to re-enter the data.

Button 4 does not specifically relate to solvent-extraction data. Rather, it allows for the calculation of solution activities and densities for multicomponent electrolyte solutions.

Data-Sheet Description

The solvent-extraction data are entered into the "Data Sheet" starting at Row 11. The user must enter the aqueous-phase volume, the organic-phase volume, the initial molar concentrations of the aqueous phase cations (e.g., H^+ , $UO_2^{2^+}$, etc.),^(a) the initial extractant (L) concentration in the organic phase, and the measured distribution coefficients. Also, if weighting factors (see Equation 11) are to be applied to the data, they must be entered here. The column headings in the Data Sheet indicate where this information is entered. After the data have been entered, clicking the "When Finished Entering Data" button will launch the application.

Modeling Procedures

As the SX Solver application is run, a number of forms or message boxes are displayed that require user input. The first form that appears after pressing the "When Finished Entering Data" button is the "Choose Extracted Metal Ion" form. This form is used to choose the cation being extracted. The choice of cations is limited to Am^{3+} , Cd^{2+} , Eu^{3+} , H^+ , Li^+ , Na^+ , Nd^{3+} , and UO_2^{2+} in Version 3.0 of the SX Solver. The user simply clicks the option button next to the appropriate cation, and then clicks the "March On" button.

After pushing the "March On" button, a dialog box appears asking the user if weighting factors are to be applied to the data. The choices are simply yes or no. After answering the question regarding weighting factors, another dialog box appears to ask if ligand activities are to be calculated. If the "no" button is clicked, all ligand activity coefficients are set equal to 1. If the "yes" button is clicked, the user must be prepared to answer the following questions:

- What is the molecular weight of the extractant?
- What is the extractant solubility parameter?
- What is the density of the extractant?
- What is the molecular weight of the diluent?
- What is the diluent solubility parameter?
- What is the density of the diluent?
- What is the density of the organic phase?
- What is the temperature?

⁽a) The current version of the SX Solver can only model nitrate systems. It is not necessary to enter the nitrate concentrations because the program will calculate them.

A good source for determining the solubility parameters is Barton (1991). The density of the diluent is generally available in the literature, but the density of the extractant and the extractant solution typically must be determined.

After inputting the appropriate information regarding ligand activities, a form appears asking the user whether to keep the previous settings. This is a useful feature when modeling data previously entered into the SX Solver application. Clicking the "Keep previous settings" option button allows for skipping several data-entry steps. However, when modeling a given set of data for the first time, the "Keep previous settings" option button should not be activated.

If the "Keep previous settings" option button is not activated, clicking the "Continue" button will activate another dialog box, which asks whether acid extraction is to be considered in the model. This must be done when significant extraction of nitric acid occurs. It should be noted that the acid-extraction constants must be determined first (see example below). If acid extraction is not a factor, simply click the "No" button. If acid extraction must be accounted for, click the "Yes" button.

Clicking "Yes" brings up the acid-extraction form. This form is used to define the various extracted acid species formed. The values of "a" and "b" for each acid species (refer to Equation 16) are entered in the form, then the "Go" button is pressed. This brings up the acid-extraction-constants form, in which the appropriate acid-extraction constants are entered. After pressing the "Submit K's" button, the "Define the Solvent Extraction Model" form appears. The values of "m," "p," and "q" (refer to Equation 1) are entered for each assumed extracted species. Also in this form are a series of check boxes corresponding to the formation of aqueous-phase M-X complexes. If one or more of these boxes is checked, the "Adjust Metal Concentration for Aqueous Phase Complexation" will subsequently be displayed, and the user will need to enter the appropriate stability constants. The "Define the Solvent Extraction Model" form also contains an option button for assuming solution ideality. Choosing this option will set all activity coefficients equal to 1. When all the necessary information is entered in the "Define the Solvent Extraction Model" form, the "Load Model" button is pushed.

At this point, the user is given an opportunity to enter a title for this modeling run. This is strictly optional. After entering the title (or not), a form appears in which the user needs to input the M-X complexation constants. This form does not appear if no M-X species were included in the model (see previous paragraph). The next form to appear is the "Enter Guesses for Extraction Constants" form. Reasonable starting guesses for the extraction constants are entered here. Finally, the "Set Up Solver" form appears. The check boxes next to each extraction constants to be varied are activated (typically, all applicable extraction constants are varied). Then the "Do It" button is pushed. This launches the application.

Once the calculation is complete, the user is taken to the "Results Sheet." This sheet displays a plot of the calculated and measured distribution coefficients. It also lists the calculated extraction constants, the correlation coefficient, the sum of the squares of the residuals, and concentrations of various species in solution. These results can be printed from this sheet.

There are three buttons at the top of the "Results Sheet." The "Change Model" button allows the user to modify the model without having to repeat the various steps listed above. Pressing the "Change Model" button will bring up the "Keep settings" form. Typically, the user activates the "Keep previous

settings" option button at this point. If not, the program will revert back several steps (to request acidextraction information). Assuming that the "Keep previous settings" option button is activated, clicking the "Continue" button will activate the "Define the Solvent Extraction Model" form. The user can change the model as needed and proceed as described above. The "Run Solver Again" button brings up the "Set Up Solver" form. This allows the user to perform further iterations. This is recommended to confirm that the model has indeed been minimized. The "Exit Program" button is self-evident.

Example: Extraction Of Nitric Acid And Uranyl Nitrate By Tetrabutylglutaramide

To demonstrate the SX Solver program, we will consider an example from the chemical literature extraction of nitric acid and uranyl nitrate by a 0.5 M solution of tetrabutylglutaramide (TBGA) in toluene (Charbonnel and Musikas 1988 and 1989).^(a) Diamide extractants of this type are of interest for their potential use in processing high-level radioactive waste.

Extraction of Nitric Acid With TBGA

To model the extraction of uranyl ion from nitric acid solutions by the TBGA extractant, it is necessary to understand the extraction behavior of nitric acid because nitric acid will consume some of the TBGA. When modeling extraction data, it is best to test various models in a logical order, starting with the simplest systems and progressing to more complicated systems as required to fit the data. This progression is illustrated for the extraction of nitric acid by 0.5 M TBGA in toluene.

Figure 2 compares the calculated and measured nitric acid distribution coefficients for 0.5 M TBGA in toluene as a function of nitrate concentration. Each plot in the figure represents different models considered, starting with a simple HNO₃•TBGA model (Figure 2a) through a four-species model (Figure 2f). Inspection of the figure clearly reveals that the best fit to the experimental data is obtained with the four-species model defined by the following equations:

$$H^{+}(aq) + NO_{3}(aq) \Leftrightarrow HNO_{3}(org)$$
 (18)

$$H^{+}(aq) + NO_{3}(aq) + TBGA(org) \Leftrightarrow HNO_{3} \bullet TBGA(org)$$
(19)

$$H^{+}(aq) + NO_{3}(aq) + 2TBGA(org) \Leftrightarrow HNO_{3} \bullet 2TBGA(org)$$
(20)

$$2H^{+}(aq) + 2NO_{3}(aq) + TBGA(org) \Leftrightarrow (HNO_{3})_{2} \bullet TBGA(org)$$
(21)

This is consistent with the conclusions made by Charbonnel and Musikas (1988). Table 2 presents the calculated extraction constants for this system.

⁽a) For the modeling results discussed here, ideality was assumed in the organic phase (i.e., organicphase activity coefficients were assigned values of one). Also, no weighting factors were applied to the data.

Extraction of Uranyl Ion With TBGA

In modeling the extraction of uranyl ion from nitric acid by 0.5 <u>M</u> TBGA in toluene, complexation of $UO_2^{2^+}$ by nitrate ion in the aqueous phase was included in the model. Only the formation of $[UO_2(NO_3)]^+$ was included. The stability constant for $[UO_2(NO_3)]^+$ varies as a function of ionic strength, and the data set examined covers a range of ionic strengths from about 0.1 to 8 <u>M</u>. Because of this, an average value of 0.26 was used for B_1 (Fuger et al. 1992).

Several models were screened to fit the data for extracting uranyl ion from nitric acid by 0.5 MTBGA in toluene. Figure 3a reveals that below $[NO_3^-] = 3 \text{ M}$, a reasonable fit to the data is achieved by assuming the formation of $UO_2(NO_3)_2 \bullet$ TBGA in the organic phase. However, this model underestimates the uranium-distribution coefficients at the higher nitrate concentrations. Adding $UO_2(NO_3)_2 \bullet$ (HNO₃) \bullet TBGA to the model (Figure 3b) yields the best fit to the data. Thus, Equations 22 and 23 best describe the extraction of uranyl ion by TBGA. Table 3 presents the extraction constants for Equations 22 and 23.

$$UO_2^{2+}(aq) + 2NO_3^{-}(aq) + TBGA(org) \Leftrightarrow UO_2(NO_3)_2 \bullet TBGA(org)$$
(22)

$$UO_{2}^{2+}(aq) + H^{+}(aq) + 3NO_{3}^{-}(aq) + TBGA(org) \Leftrightarrow UO_{2}H(NO_{3})_{3} \bullet TBGA(org)$$
(23)

Equation 23 can be reformulated as the extraction of $[UO_2(NO_3)_3]^-$ by the protonated diamide:

$$[UO_2(NO_3)_3]^{-}(aq) + [H \bullet TBGA]^{+}(org) \Leftrightarrow UO_2(NO_3)_3 \bullet H \bullet TBGA(org)$$
(24)

Charbonnel and Musikas (1989) reported spectral evidence for the existence of the $[UO_2(NO_3)_3]^-$ ion in the organic phase in this extraction system. So the modeling result corroborates the earlier reported spectral results.

Extracted Specie	$\mathbf{K}^{(a)}$	
HNO ₃	0.00065 ± 0.00009	
HNO ₃ •TBGA	0.517 ± 0.017	
HNO ₃ •2TBGA	0.896 ± 0.079	
(HNO ₃) ₂ •TBGA	0.0272 ± 0.0009	
 (a) The reported uncertainties represent the standard deviations as determined using the Microsoft Excel® macro developed by Billo (1997). The correlation coefficient for this model was 0.974. 		

Table 2.	Calculated Extraction Constants For the
	Extraction of Nitric Acid With TBGA

	K ^(a)	
Extracted Specie	K	
UO ₂ (NO ₃) ₂ •TBGA	82.1 ± 6.3	
UO ₂ H(NO ₃) ₃ •TBGA	0.441 ± 0.083	
(a) The reported uncertainties represent the		
standard deviations as determined using the		
Microsoft Excel® macro developed by		
Billo (1997). The correlation coefficient		
for this model was 0.980.		

Table 3. Calculated Extraction Constants for the Extraction of U(VI) with TBGA



Figure 2. Extraction of Nitric Acid With 0.5 M TBGA in Toluene: Comparison of Measured and Calculated Values. The models considered were a) HNO₃·TBGA, b) HNO₃·2TBGA, c) (HNO₃)₂·TBGA, d) HNO₃·TBGA plus (HNO₃)₂·TBGA, e) HNO₃·TBGA plus HNO₃·2TBGA plus (HNO₃)₂·TBGA, and f) HNO₃ plus HNO₃·TBGA plus HNO₃·2TBGA plus (HNO₃)₂·TBGA.



Figure 3. Extaction of Uranyl Ion with 0.5 M TBGA in Toluene: Comparison of Measured and Calculated Values. The models considered were a) UO₂(NO₃)₂·TBGA and b) UO₂(NO₃)₂·TBGA plus UO₂H(NO₃)₃·TBGA

Future Developments

Although Version 3.0 is a major upgrade of the SX Solver, the current version still has a number of limitations, including the following:

- Only a limited number of electrolytes is included, and only nitrate systems can be considered.
- Mixed extractants cannot be considered, e.g., synergistic solvent mixtures.
- Aggregation of the extractant cannot be explicitly considered.
- Improved output capabilities are needed.

Future versions of the program will include enhancements to address these limitations.

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