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## **The SX Solver: A New Computer Program for Analyzing Solvent- Extraction Equilibria**

G. J. Lumetta  
B. K. McNamara  
B. M. Rapko

January 1999

Prepared for the U.S. Department of Energy  
under Contract DE-AC06-78RLO 1830

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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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# Contents

Summary .....	iii
Acknowledgements .....	iii
Introduction .....	1
Model Description .....	3
Program Description .....	5
Example: Extraction Of Nitric Acid By Tributyl Phosphate .....	6
Future Developments .....	9
References .....	11

## Introduction

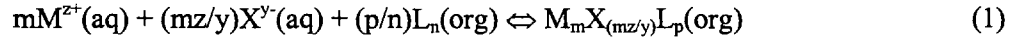
Equilibria phenomena are of central importance to solvent-extraction science (Rydberg et al. 1992). Such phenomena have been investigated for many decades. Two primary methods are employed in studying solvent-extraction equilibria—graphical methods (slope analysis) and numerical methods (computer modeling). Despite the widespread availability of computers, graphical methods are still extensively used. A review of the journal *Solvent Extraction and Ion Exchange* for 1997 revealed a fairly even split between papers in which numerical methods were used versus papers in which slope analysis was used—13 papers using numerical methods versus 12 using slope analysis. For many of the papers that used numerical methods, unspecified curve-fitting routines were used to model specific equilibrium expressions. The following computer programs have been designed specifically for analyzing solvent-extraction equilibria: LETAGROP-DISTR (Liem 1971), MODEX (Noirot and Wozniak 1985), and SXLSQA (Baes et al. 1990).

We have been developing a program using the “Solver” function in Microsoft Excel® to analyze solvent-extraction equilibria. Because the program revolves around the Solver function, we have named the program the “SX Solver.” The Solver function has previously been successfully employed in solvent-extraction technology, namely in the Generic TRUEX Model (GTM) (Vandegrift et al. 1990). The GTM has a considerable level of sophistication, but it is primarily a tool for process and flowsheet design. The program we are developing is designed to model solvent-extraction equilibria at a fundamental level. The SX Solver program takes advantage of the graphical user-interface of Excel®, so it is designed to be user-friendly. This paper describes the basis for this program and an example of its use.



## 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).



The equilibrium constant for this reaction is defined as

$$K = \frac{y_C [M_m X_{(mz/y)} L_p]_o}{(y_M [M^{z+}]_a)^m (y_X [X^{y-}]_a)^x (y_L [L_n]_o)^{(p/n)}} \quad (2)$$

where  $y_C$ ,  $y_M$ ,  $y_X$ , and  $y_L$  are the molar-scale activity coefficients for  $M_mX_{(mz/y)}L_p$ ,  $M^{z+}$ ,  $X^{y-}$ , and  $L_n$ , respectively; and  $x = mz/y$ . 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. 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:

$$D = \frac{[M]_o}{[M]_a} = \frac{m[M_m X_{(mz/y)} L_p]_o}{[M^{z+}]_a} \quad (3)$$

It should be noted that  $[M^{z+}]_a$  represents the total metal concentration in aqueous phase. This is a simplification because aqueous phase complexation of the metal ion (e.g., by nitrate ion) is not taken into account. The result of this simplification is that the binding constants for metal complexation in the aqueous phase are incorporated into the calculated extraction constants. Combining Equations 2 and 3 gives

$$K = \frac{y_C}{y_M^m y_X^x y_L^{(p/n)}} \cdot \frac{D}{m[M^{z+}]_a^{m-1} [X^{y-}]_a^x [L_n]_o^{(p/n)}} \quad (4)$$

Rearranging Equation 4 gives

$$D = \frac{y_M^m y_X^x y_L^{(p/n)}}{y_C} \cdot mK [M^{z+}]_a^{m-1} [X^{y-}]_a^x [L_n]_o^{(p/n)} \quad (5)$$

If more than one extraction equilibrium (of the type shown in Eq. 1) is involved, Equation 3 becomes

$$D = \frac{\sum_i m_i [M_{m_i} X_{x_i} L_{p_i}]_o}{[M^{z+}]_a} \quad (6)$$

and Equation 5 becomes

$$D = \frac{\sum_i \frac{y_M^{m_i} y_X^{x_i} y_L^{(p_i/n)}}{y_{C_i}} \cdot m_i K_i [M^{z+}]_a^{m_i} [X^{y-}]_a^{x_i} [L_n]_o^{(p_i/n)}}{[M^{z+}]_a} \quad (7)$$

where  $K_i$  is the extraction constant for species  $i$ .

## Program Description

Equation (7) 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:

$$SSR = \sum w(D - D_{\text{calcd}})^2 \quad (8)$$

where  $D$  and  $D_{\text{calcd}}$  are the measured and calculated distribution coefficients, respectively, for a given measurement; and  $w$  is a weighting factor defined by the user.  $D_{\text{calcd}}$  is determined through Equation 7.

In the current version of the SX Solver program, it is generally assumed that the concentration of the extracted cation,  $M^{z+}$ , is much lower than the concentration of the counter anion,  $X^{y-}$ . That is, a supporting electrolyte is used to buffer the system. Preferably, experiments should be designed so that changes in the aqueous phase  $X^{y-}$  concentration, due to coextraction with the metal ion, are less than 5%. It is also assumed that the cation of the supporting electrolyte is not extracted to any extent. Under these conditions, the aqueous phase can be treated as a solution of a single electrolyte. The activity coefficient for the anion,  $y_X$ , is then primarily defined by the activity of the supporting electrolyte. The aqueous-phase activity coefficients are determined using the method established by Bromley (1973). For this calculation, molar concentrations are converted to molal concentration 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):  $y_{\pm} = \gamma_{\pm} m d_0 / c$ , where  $\gamma_{\pm}$  is the molal-scale activity coefficient,  $m$  is the molal concentration,  $c$  is the molar concentration, and  $d_0$  is the density of water (0.9971 g/mL at 25°C). Currently, the program only supports activity calculations for  $\text{NaNO}_3$ ,  $\text{LiNO}_3$ ,  $\text{HNO}_3$ , and  $\text{NaCl}$  as the supporting electrolytes, but subsequent versions of the program will incorporate activity calculations for other electrolytes. The activity coefficient for  $M^{z+}$  is assumed to be unity under these conditions; in the extraction experiments, the concentration of  $M^{z+}$  should be kept low enough that this assumption is valid.

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). Reference 4 provides a description of the procedure used to calculate the ligand-activity coefficients. 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 ( $y_C$ ) are assumed to be one.

It is assumed that all of the extractant remains in the organic phase. That is, the extractant is assumed to have no appreciable solubility in the aqueous phase. The extractant concentration indicated in Equation 7,  $[L_n]_o$ , refers to the organic-phase concentration of the aggregated (if applicable) extractant. This is related to the concentration of the free extractant,  $[L]_o$ , by the following equation:

$$[L_n]_o = K_{agg}[L]_o^n \quad (9)$$

where  $K_{agg}$  is the equilibrium constant for the aggregation reaction.<sup>(a)</sup> The following mass balance expression applies to the extractant concentration:

$$\sum_i \frac{y_M^{m_i} y_X^{x_i} y_L^{(p_i/n)}}{y_{C_i}} \cdot p_i K_i [M^{z+}]_a^{m_i} [X^{y-}]_a^{x_i} (K_{agg})^{(p_i/n)} [L]_o^{p_i} + [L]_o - [L]_{tot} = \quad (10)$$

where  $[L]_{tot}$  is the total analytical concentration of the extractant in the organic phase. The SX Solver program uses Newton's method of approximation to solve Equation 10 for the value of  $[L]_o$ . This is achieved by applying Equation 11. A reasonable initial value is:

$$[L]_o = [L]_o^* - \frac{f([L]_o^*)}{f'([L]_o^*)} \quad (11)$$

chosen for  $[L]_o$  (in this case  $[L]_{tot}$  is used as the initial value). The function,  $f([L]_o)$ , is then calculated according to Equation 10; the function  $f'([L]_o)$  is the derivative of Equation 10 with respect to  $[L]_o$ . A new value for  $[L]_o$  is obtained by Equation 11. This new value is assigned as  $[L]_o$ , and the process is repeated until there is no significant change between  $[L]_o$  and  $[L]_o$ . The resulting value of  $[L]_o$  is then applied to Equations 7 and 9.

In running the program, the user supplies the following information:

- the components initially present in the aqueous phases and their concentrations (in moles/L)
- the component of interest; that is, the metal ion that is being extracted
- the values for  $z+$ ,  $y-$ , and  $n$  (the extractant aggregation number)
- the number of extracted species—up to five species are currently supported
- $m_i$  and  $p_i$  values for each extracted species
- initial values for the  $K_i$ .

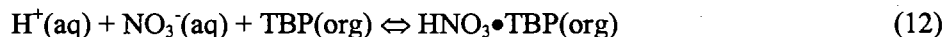
The user is prompted in a logical manner for these inputs. If the user chooses, default values as specified from previous calculations can be used for certain inputs. This feature is advantageous because it allows for rapid screening of a number of possible models on a given data set. The Excel® Solver is applied to vary the  $K_i$  values until the function in Equation 8 is minimized. The user can save the results in an Excel® spreadsheet for future reference or use.

### Example: Extraction Of Nitric Acid By Tributyl Phosphate

To demonstrate the SX Solver program, we will consider an example from the chemical literature—extraction of nitric acid by hydrocarbon solutions of tributyl phosphate (TBP). This system is of industrial importance with respect to reprocessing nuclear fuel (Büchner et al. 1989).

<sup>(a)</sup> For the current version of SX Solver, prior knowledge of the value of  $K_{agg}$  is preferable. Otherwise, the user must manually adjust  $K_{agg}$  to determine the effects of aggregation.

For aqueous HNO<sub>3</sub> concentrations of less than 9 M, the extraction of HNO<sub>3</sub> by TBP can be described by two extraction equilibria (Chaiko and Vandegrift 1988):



It is assumed that the solubility of TBP in the aqueous phase is zero, and, likewise, the solubility of HNO<sub>3</sub> in the hydrocarbon diluent is zero.

The data for the TBP extraction of HNO<sub>3</sub> were taken from Davis (1962). These data were modeled according to Equations 12 and 13 using the SX Solver program. It should be noted that in this example, there is no supporting electrolyte. The program allows for the calculation of the aqueous phase nitric acid activities at each data point. The organic-phase activity coefficients were assigned the values of 1. This, of course, is not true, but for a given total TBP concentration, it can be assumed that the term  $y_L^{(p/n)}/y_C$  is constant. The data were divided into five sets for the modeling calculation—one set for each total TBP concentration. The program calculated the values of  $K_{1,1}$  and  $K_{1,2}$  for each data set;  $K_{1,1}$  is the equilibrium constant for Equation 12, and  $K_{1,2}$  is the equilibrium constant for Equation 13. Table 1 presents the calculated extraction constants for Reactions 12 and 13; analogous values from the literature (Chaiko and Vandegrift 1988) are also reported in Table 1. Figure 1 compares the experimental and calculated HNO<sub>3</sub> extraction isotherms. Clearly, good agreement exists between the experimental and calculated values as indicated by correlation coefficients  $\geq 0.995$ . The extraction constants determined in this manner are similar to those reported in the literature, but there are some discrepancies. The discrepancies may be due to differences in the manner in which the aqueous-phase HNO<sub>3</sub> activities were determined. Also, the molar TBP concentrations used in Chaiko and Vandegrift (1988) were slightly different than those used here. This is because Chaiko and Vandegrift adjusted the concentrations originally listed by Davis (1962) to avoid potential problems associated with extracted water. We used the concentrations given by Davis, without adjustment. Presumably, nonideality effects in the organic phase are responsible for the changes in the  $K_{1,1}$  and  $K_{1,2}$  values for different TBP concentrations.

**Table 1.** Extraction of Nitric Acid by Tributyl Phosphate<sup>(a)</sup>

[TBP(org)] <sub>tot</sub>		This Work		Chaiko and Vandegrift (1988)		$r^{(b)}$
vol %	mole/L	$K_{1,1}$	$K_{1,2}$	$K_{1,1}$	$K_{1,2}$	
5	0.17	0.20	0.59	0.13	0.77	0.999
10	0.35	0.25	0.43	0.18	0.46	0.999
15	0.52	0.25	0.52	0.17	0.53	0.995
30	1.09	0.24	0.48	0.19	0.43	0.996
65	2.33	0.19	0.40	0.15	0.33	0.999

(a) Experimental data taken from Davis (1962); TBP dissolved in Amsco 125-82.

(b) The correlation coefficient for the calculations done here.

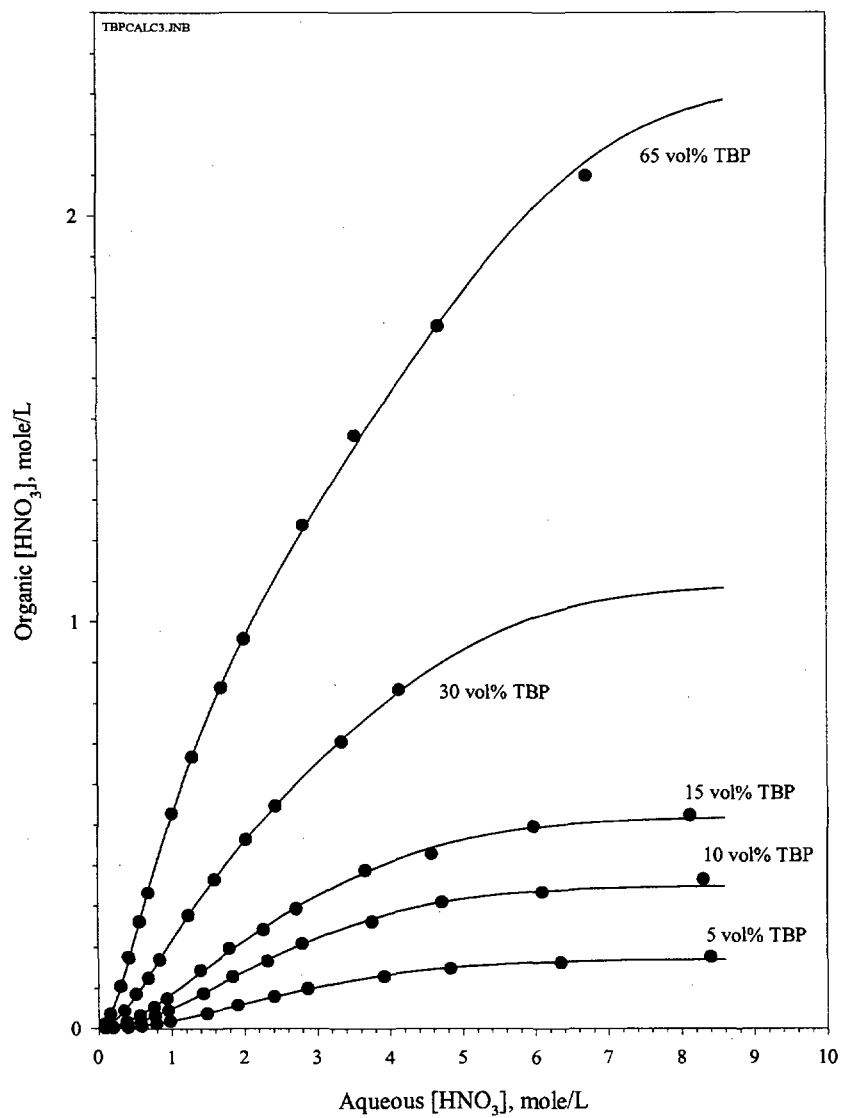


Figure 1. Extraction of HNO<sub>3</sub> With TBP: Comparison of Experimental and Calculated Values

## Future Developments

The current version of the SX Solver program has the following limitations:

- only a limited number of supporting electrolytes is included
- activity coefficients for mixed electrolyte systems cannot be calculated
- only the extraction of one cation can be considered
- mixed extractants cannot be considered, e.g., synergistic solvent mixtures
- explicit corrections cannot be made for aqueous-phase metal complexation
- if the extractant is aggregated, prior knowledge of the aggregation constant is needed; otherwise manual adjustment of the extraction constant is required
- improved output capabilities are needed.

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

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