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Modeling of the Simultaneous Extraction of Nitric Acid and Uranyl Nitrate with Tri-*n*-butyl Phosphate. Application to Extraction Operation

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ABSTRACT

A mathematical model developed for the equilibrium HNO_3–$UO_2(NO_3)_2$–tri-*n*-butyl phosphate (TBP)–diluent is the basis of the computation of distribution isotherms. The isotherms are used to study the influence of TBP concentration on two chosen operation parameters, distribution coefficients and number of theoretical stages, for the selected flow sheets. It is established that an increase in TBP concentration leads to a decrease in the number of theoretical stages for the extraction flow sheets but to their increase for the stripping flow sheets. Given diagrams can be used to determine the efficiency of extraction processes. Agreement with available literature calculations on the number of theoretical stages supports the use of our model in the computation of distribution isotherms, of the system quoted above, in a wide range of nitric acid, uranyl nitrate, and TBP concentrations.

INTRODUCTION

Stoichiometric equilibrium constants of solvent extraction of nitric acid and uranyl nitrate with tri-*n*-butyl phosphate (TBP) cannot characterize the extraction isotherm in the whole range of nitric acid, uranyl nitrate, and TBP concentrations. Thermodynamic equilibrium constants, involving activities of the interacting species, would be a solution. Although the mean activity

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coefficients of nitric acid and uranyl nitrate in the aqueous phase are available, knowledge of their organic-phase activities is still unsatisfactory. As a consequence, a complete thermodynamic description of the distribution equilibrium has been difficult to realize. Development of empirical calculation methods based on a sound choice of parallel chemical reactions can be a good approach.

Basic research dealing with enhancement of efficiency of the solvent extraction of uranyl nitrate (from nitric acid solution) with TBP has been founded on creation of corresponding chemical models. Nikolaeva et al. (1) offered a model based on the species $HNO_3 \cdot TBP$, $HNO_3 \cdot 2H_2O \cdot 2TBP$, $HNO_3 \cdot 3TBP$, $2HNO_3 \cdot 3H_2O \cdot TBP$, $UO_2(NO_3)_2 \cdot 2TBP$, and $UO_2(NO_3)_2 \cdot 3TBP$ existing in the organic phase. The initial concentrations (on the molality scale) were $m_{H^+} = 0.3–11$; $m_{UO_2^{2+}} = 0.4–4.4$; $m_{NO_3^-} = 3.6–14.0$, and pure TBP. They used activity coefficients of electrolytes and water activity. The error of fitting was 15%. Rozen and Andrutskii (2) described the simultaneous extraction of nitric acid and uranyl nitrate as the extraction of nitric acid complexes, $(HNO_3)_i$, by uranyl nitrate disolvate, $UO_2(NO_3)_2 \cdot 2TBP$. Here, $i = 2$, 3, and 4 up to 15 $mol \cdot dm^{-3}$ nitric acid. The authors think that $UO_2(NO_3)_2 \cdot 2TBP$ is a relatively effective extractant for nitric acid and metals. Extraction of uranyl nitrate with TBP from 0.01–10 $mol \cdot dm^{-3}$ nitric acid solutions has been modeled using the SXLSQA program for treatment of solvent extraction equilibria (3).

Development of empirical calculation methods, yielding apparent concentration equilibrium constants or distribution ratios as a function of different concentration variables, involving TBP in an alkane diluent and uranyl nitrate or nitric acid in the aqueous phase, was referred to by Kolarik (4).

Mokili and Poitrenaud (5) described the extraction of nitric acid and water with 10–100% TBP in dodecane. They found the existence of the following species in the organic phase: TBP, $TBP \cdot H_2O$, $HNO_3 \cdot H_2O$, $TBP \cdot HNO_3$, $(TBP)_2 \cdot HNO_3 \cdot H_2O$, and $TBP \cdot (HNO_3)_2$. An extensive review of the corresponding literature is also given.

A set of stoichiometric constants expressions of the equilibria involved in the system $HNO_3–UO_2(NO_3)_2$–TBP–diluent is the basis of the mathematical model we developed (6, 7, and the references therein). The model gives relatively simple relationships for the simultaneous distribution of nitric acid and uranyl nitrate for a wide range of TBP concentrations. These equations make it possible to predict distribution data for the extraction system of particular interest in uranium processing technology and in reprocessing of spent nuclear fuel. Computation of the steady-state concentrations, distribution coefficients, and the number of theoretical stages permits determination of the efficiency of extraction processes and the choice of the proper variant for nitric acid and uranyl nitrate distribution in a countercurrent apparatus.

The aim of this work is to show the application of the model to nitric acid and uranyl nitrate separately as well as simultaneous extraction with TBP, and to their stripping from the organic phase by aqueous solutions of nitric acid. Computed theoretical isotherms enable investigation of the influence of TBP concentrations on two chosen operation parameters, distribution coefficients and the number of theoretical stages, for the selected flow sheets.

THE MODEL

Simultaneous extraction of nitric acid and uranyl nitrate from aqueous solutions with TBP dissolved in a hydrocarbon diluent can be modeled by means of Equilibria (1)–(4) and the corresponding equilibrium constants Expressions (5)–(8).

$$2\mathrm{S} \Leftrightarrow \mathrm{D} \tag{1}$$

$$\mathrm{H}^+ + \mathrm{NO}_3^- + \mathrm{S} \Leftrightarrow \mathrm{HNO}_3{\cdot}\mathrm{S} \tag{2}$$

$$\mathrm{H}^+ + \mathrm{NO}_3^- + \mathrm{D} \Leftrightarrow \mathrm{HNO}_3{\cdot}\mathrm{D} \tag{3}$$

$$\mathrm{UO}_2^{2+} + 2\mathrm{NO}_3^- + 2\mathrm{S} \Leftrightarrow \mathrm{UO}_2(\mathrm{NO}_3)_2{\cdot}2\mathrm{S} \tag{4}$$

$$Q_\mathrm{D} = C_\mathrm{D}/C_\mathrm{S}^2 \tag{5}$$

$$Q_{\mathrm{HN\cdot S}} = C_{\mathrm{HN\cdot S}}/AC_\mathrm{S} \tag{6}$$

$$Q_{\mathrm{HN\cdot D}} = C_{\mathrm{HN\cdot D}}/AC_\mathrm{D} \tag{7}$$

$$Q_{\mathrm{UN\cdot 2S}} = C_{\mathrm{UN\cdot 2S}}/BC_\mathrm{S}^2 \tag{8}$$

where $A = a_\mathrm{H}a_\mathrm{N} = C_\mathrm{H}^2 y_{\pm(\mathrm{HN})}^2$ and $B = a_\mathrm{U}a_\mathrm{N}^2 = 4[C_\mathrm{U} y_{\pm(\mathrm{UN})}]^3$. S and D denote TBP monomer and dimer, respectively, and C is related to the mol·dm^{-3} concentration of the species identified in the subscripts. S, D, HN·S, HN·D, and UN·2S refer to species in the organic phase, while H^+, NO_3^-, and UO_2^{2+} denote ions present in the aqueous phase. $y_\pm$ is the activity coefficient of ions in the aqueous phase at standard state infinite dilution. Higher solvates of nitric acid, $\mathrm{HNO}_3{\cdot}2\mathrm{S}$ and $\mathrm{HNO}_3{\cdot}3\mathrm{S}$, have not been considered since the equilibrium treated in this work does not contain more than 2 mol·dm^{-3} of nitric acid.

Equations (5)–(8) and the mass balance Eq. (9) (C_TBP denotes the total concentration in the organic phase) lead to a quadratic equation whose solution for C_S is Eq. (10).

$$C_\mathrm{TBP} = C_\mathrm{S} + 2C_\mathrm{D} + 2C_{\mathrm{HN\cdot D}} + C_{\mathrm{HN\cdot S}} + 2C_{\mathrm{UN\cdot 2S}} \tag{9}$$

$$C_\mathrm{S} = \frac{\sqrt{(1 + AQ_{\mathrm{HN\cdot S}}) + 8C_\mathrm{TBP}[BQ_{\mathrm{UN\cdot 2S}} + Q_\mathrm{D}(1 + AQ_{\mathrm{HN\cdot D}})]} - 1 - AQ_{\mathrm{HN\cdot S}}}{4[BQ_{\mathrm{UN\cdot 2S}} + Q_\mathrm{D}(1 + AQ_{\mathrm{HN\cdot D}})]} \tag{10}$$

The concentrations of free TBP monomer obtained in the organic phase enable us to calculate the total concentrations of nitric acid and uranyl nitrate in the organic phase according to Eq. (11) and (12).

$$C^{\mathrm{tot}}_{\mathrm{HNO_3(org)}} = C_{\mathrm{HN\cdot S}} + C_{\mathrm{HN\cdot D}} = AC_{\mathrm{S}}(Q_{\mathrm{HN\cdot S}} + Q_{\mathrm{D}}C_{\mathrm{S}}) \tag{11}$$

$$C^{\mathrm{tot}}_{\mathrm{UN(org)}} = C_{\mathrm{UN\cdot 2S}} = BQ_{\mathrm{UN\cdot 2S}}C^2_{\mathrm{S}} \tag{12}$$

The apparent constant values of Q_{D}, $Q_{\mathrm{HN\cdot D}}$, $Q_{\mathrm{HN\cdot S}}$, and $Q_{\mathrm{UN\cdot 2S}}$ are obtained as the best fit of the experimental data on $C_{\mathrm{HN(aq)}}$, $C_{\mathrm{UN(aq)}}$, $C^{\mathrm{tot}}_{\mathrm{HN(org)}}$, and $C^{\mathrm{tot}}_{\mathrm{UN(org)}}$ with Eqs. (5)–(8) and (10)–(12). Distribution data, calculated from Eqs. (11) and (12), deviate from the experimental data by 8.7%. This is a fully satisfactory fit because the model parameters have been obtained from experimental data originating from different sources. Details are given in the previous paper (7). Theoretical isotherms can be calculated according to the described model, for the next apparent constants values (7): $Q_{\mathrm{D}} = 0.039$, $Q_{\mathrm{HN\cdot D}} = 14.39$, $Q_{\mathrm{HN\cdot S}} = 0.058$, and $Q_{\mathrm{UN\cdot 2S}} = 130$. The proposed model has been verified for the extraction of 0.1–15 mol·dm^{-3} nitric acid with 10–100% TBP, 0.1–1.4 mol·dm^{-3} uranyl nitrate with 10–60% TBP, and simultaneous extraction of 0.1–4.0 mol·dm^{-3} nitric acid and 0.1–1.2 mol·dm^{-3} uranyl nitrate with 5–30% TBP in a hydrocarbon diluent.

APPLICATION OF THE MODEL

The distribution coefficient of uranyl nitrate, defined as $q_{\mathrm{U}} = C_{\mathrm{U(org)}}/C_{\mathrm{U(aq)}}$, is derived from Eq. (8) and $C_{\mathrm{N}} = 2C_{\mathrm{U}}$ as given in Eq. (13).

$$q_{\mathrm{U}} = 4Q_{\mathrm{UN\cdot 2S}}C^2_{\mathrm{UN}}[y^{\mathrm{(HN)}}_{\pm\mathrm{(UN)}}]^3C^2_{\mathrm{S}} \tag{13}$$

The value of C_{S} is calculated from Eq. (10). Here, $y^{\mathrm{(HN)}}_{\pm\mathrm{(UN)}}$ denotes the mean activity coefficient of uranyl nitrate (subscript) in the presence of nitric acid (superscript) and is calculated according to Goldberg et al. (8). The influence of nitric acid on Equilibrium (4) is involved in the $y^{\mathrm{(HN)}}_{\pm\mathrm{(UN)}}$ value.

Figure 1 shows that uranyl nitrate distribution data (nitric acid absent and $C_{\mathrm{TBP}} =$ constant) have a maximum which describes the optimum q_{U} values. In the case of simultaneous extraction of nitric acid and uranyl nitrate, when $C_{\mathrm{TBP}} =$ constant, an extreme value of q_{U} does not exist.

Separate Extraction and Stripping of Uranyl Nitrate or Nitric Acid

The influence of C_{TBP} on the number of theoretical stages, N_{T}, for the extraction and stripping of nitric acid or uranyl nitrate under selected operating

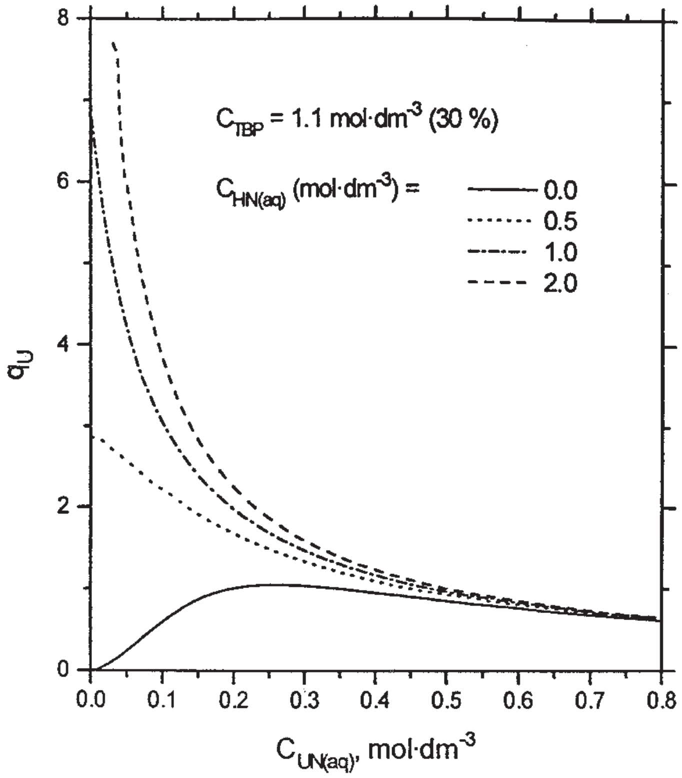


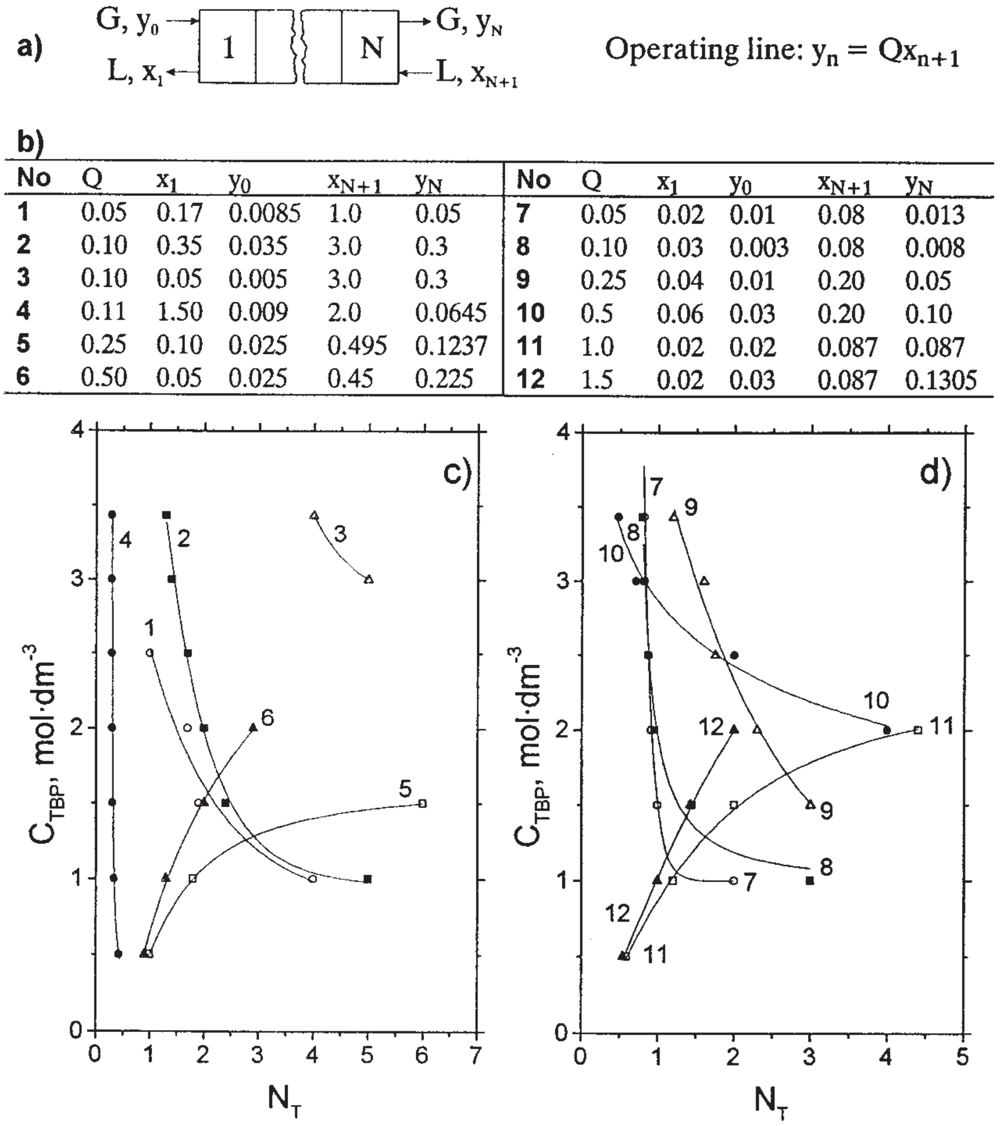
FIG. 1 Distribution coefficient values of uranyl nitrate for C_{TBP} = constant and different equilibrium concentrations of nitric acid calculated by means of Eqs. (13) and (10).

conditions has been investigated. The results obtained, based on theoretical isotherms computed according to our model, are shown in Fig. 2. As can be seen, an increase in C_{TBP} concentration leads to a decrease in N_T in the case of the extraction operation but to an increase in the case of the stripping operation. The extreme of N_T values (optimum value) does not exist. Therefore, for the same extraction flow sheet, an increase in C_{TBP} concentration gives rise to a decrease in the length or height of the extraction unit. In the case of the stripping flow sheet, the C_{TBP} concentration effect is the contrary.

Simultaneous Extraction and Stripping of Nitric Acid and Uranyl Nitrate

In order to investigate the influence of the total concentration of TBP on the number of theoretical stages for the system HNO_3–$UO_2(NO_3)_2$–TBP–diluent, two flow sheets (extraction and stripping) have been selected. Here, the ratio of the aqueous to the organic flow (Q) is assumed to be constant.

In the extraction flow sheet, taken from the literature (9), $Q = 1.43$, the concentration of uranyl nitrate in the aqueous and the organic inlet flow is 0.30



No	Q	x_1	y_0	x_{N+1}	y_N	No	Q	x_1	y_0	x_{N+1}	y_N
1	0.05	0.17	0.0085	1.0	0.05	**7**	0.05	0.02	0.01	0.08	0.013
2	0.10	0.35	0.035	3.0	0.3	**8**	0.10	0.03	0.003	0.08	0.008
3	0.10	0.05	0.005	3.0	0.3	**9**	0.25	0.04	0.01	0.20	0.05
4	0.11	1.50	0.009	2.0	0.0645	**10**	0.5	0.06	0.03	0.20	0.10
5	0.25	0.10	0.025	0.495	0.1237	**11**	1.0	0.02	0.02	0.087	0.087
6	0.50	0.05	0.025	0.45	0.225	**12**	1.5	0.02	0.03	0.087	0.1305

FIG. 2 (a) Schematic of the assumed countercurrent array: Q denotes the ratio of aqueous (L) to organic (G) flow. x and y are the concentrations, in mol·dm^{-3}, of the aqueous and the organic phases, respectively, at the ends of the extractor. 1 and N are the end stages, and n is the current stage of the extractor. (b) Operating parameters used for the calculation of the number of theoretical stages, N_T, for different concentrations of C_{TBP}, for the extraction and stripping of uranyl nitrate (c) or nitric acid (d). Numbers beside the curves correspond to the numbers in the columns headed by ''No.''

and 0.048 mol·dm^{-3}, while in the outlet flow it is 0.02 and 0.448 mol·dm^{-3}, respectively. The concentration of nitric acid in the aqueous and the organic inlet flow is 2.00 and 0.00 mol·dm^{-3}, respectively. Owing to the change in C_{TBP}, the concentrations of nitric acid in the aqueous and the organic outlet flows is changeable.

In the stripping flow sheet, $Q = 2.0$, the concentration of uranyl nitrate in the aqueous and the organic inlet flow is 0.00 and 0.20 mol·dm^{-3}, and in outlet flow is 0.10 and 0.00 mol·dm^{-3}, respectively, whereas the concentration of nitric acid in the aqueous and the organic inlet flows is 0.01 mol·dm^{-3}. As assumed, the concentration of nitric acid in the aqueous and the organic flows is 0.10 and 0.00 mol·dm^{-3}, respectively.

Our consideration of the influence of C_{TBP} on N_{T} for the selected flow sheets is based on theoretical isotherms computed from the chemical model, Eqs. (11) and (12), as explained in the Model Section. The theoretical stages obtained for the system investigated are shown in Fig. 3. As can be seen, an increase in C_{TBP} leads to a decrease in N_{T} for the extraction flow sheet but to an increase in N_{T} for the stripping flow sheet. This is in accordance with the results obtained for one-component extraction (cf. Fig. 2). Therefore, an increase in C_{TBP} leads to a decrease in the length or height of an extraction unit. Figure 3 also includes the N_{T} value for 30% TBP, calculated in the

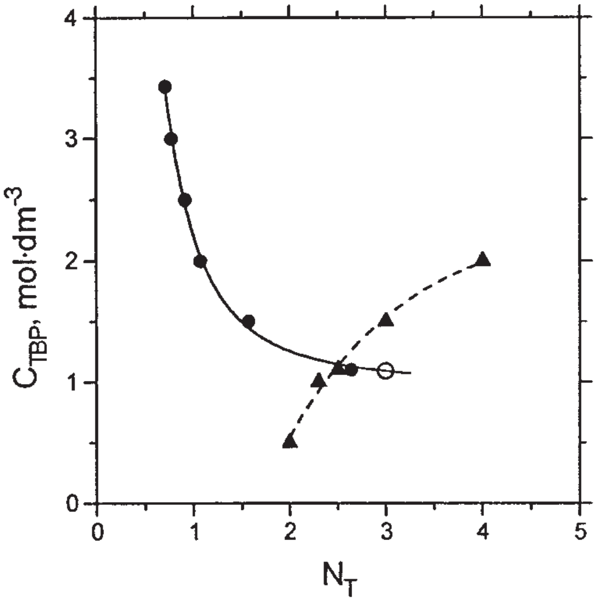


FIG. 3 The number of theoretical stages, N_{T}, for different concentrations of C_{TBP} in the simultaneous extraction (full line) and stripping (dashed line) of nitric acid and uranyl nitrate. Solid circles and triangles are the results of our calculations, and the open circle denotes the result taken from the literature (9).

literature (9), which falls on the curve. It supports our model as used in the computation of distribution isotherms for the simultaneous extraction of nitric acid and uranyl nitrate with TBP in a wide range of nitric acid, uranyl nitrate, and TBP concentrations.

CONCLUSION

The equilibria involved in the system H_2O–HNO_3–$UO_2(NO_3)_2$–TBP–diluent have been successfully modeled to predict simultaneous nitric acid and uranyl nitrate extraction with TBP. We have introduced mutual nitric acid and uranyl nitrate activities in the aqueous phase and a reliable choice of the species existing in the organic phase: TBP, $(TBP)_2$, $(TBP)_2 \cdot HNO_3$, $TBP \cdot HNO_3$, $TBP \cdot 2HNO_3$, $TBP \cdot 3HNO_3$, and $UO_2(NO_3)_2 \cdot 2TBP$. The water in the organic phase has been considered as solubilized water, as explained in previous work (7). Neglecting the influence of water on this extraction equilibrium does not invalidate the model.

The model gives a good fit to the experimental data found in the literature with a relative standard deviation of 8.7%. According to our knowledge, it is a unique model which explains the simultaneous extraction of nitric acid and uranyl nitrate with TBP in a wide range of their concentrations.

Computation of steady-state concentrations, distribution coefficients, and the number of theoretical stages permits determination of the efficiency of uranium processing technology and the reprocessing of spent nuclear fuel. It enables selection of the proper variant for nitric acid and uranyl nitrate distribution in countercurrent apparatus.

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