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PREDICTION OF PHASE EQUILIBRIA IN TRIBUTYL PHOSPHATE EXTRACTION SYSTEM USING THE UNIFAC GROUP CONTRIBUTION METHOD *

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ABSTRACT

Vapour–liquid and vapour–liquid–liquid equilibria of 19 tributyl phosphate-involved systems are experimentally studied. The activity coefficients of aqueous species are calculated using Pitzer's equations. For the organic phase, the UNIFAC method is used for the correlation of the experimental data and the prediction of the equilibrium composition. For extraction systems of HNO_3 and $UO_2(NO_3)_2$, a group assignment is proposed. Parameters needed in the method are derived or determined by data regression. Concentrations predicted by UNIFAC are in good agreement with the experimental results.

INTRODUCTION

A continuous effort has been made by the chemists and engineers engaged in the field of solvent extraction to predict phase equilibria [1]. Different kinds of solution theories and semi-empirical methods of correlation have been used to express the non-ideality of a liquid mixture, and to calculate the partition of a particular component between the aqueous phase and the organic phase in a solvent extraction system. For electrolyte solutions we now have effective equations such as Pitzer's [2,3] to estimate the activity coefficient of an aqueous species. A fairly good precision can be obtained when using these equations even for a multicomponent electrolyte mixture and in rather high concentrations. For multicomponent non-electrolyte mixtures, some semi-empirical models such as the models of Wilson [4], NRTL [5], UNIQUAC [6], and UNIFAC [7] are usually used for data correlation and equilibrium prediction.

The UNIFAC method, being based on the group contribution concept, has the advantage that it can be used in the calculation of a multicomponent

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system with a small number of parameters. This superiority becomes clearer when the number of components increases. It is evident that this kind of model is suitable for correlating the property of the organic phase in an industrial solvent extraction system, of which the composition is usually complicated.

In this work, we take a well-known solvent extraction system as an example and use the UNIFAC method to correlate the equilibrium. In this system, the extractant is tributyl phosphate (TBP), and the material to be extracted is nitric acid or uranyl nitrate. The extraction of HNO_3 and $UO_2(NO_3)_2$ by TBP is the most important step in the processing of nuclear fuels. There has been a great many studies devoted to this process. Some authors used empirical equations to express its apparent equilibrium constant [8–10], but they all avoided the direct calculation of the activity coefficients of the components in both phases. Rozen [11] studied the vapour–liquid equilibrium of some TBP-containing binary systems, and correlated the experimental data using the UNIFAC equation, but no further work has been reported. This work can be a test of the feasibility of the UNIFAC method for this kind of system.

EXPERIMENTAL

For the liquid–liquid extraction systems, the aqueous phase, i.e. a solution of HNO_3 or $UO_2(NO_3)_2$ in different concentrations, and the organic phase, i.e. a solution of TBP in heptane (with an initial TBP concentration of 15, 35, 50, 66, 83, 100 vol.%) were added to the equilibrium tubes, which were shaken in a thermostatted box for 30 min and then centrifuged to separate the phases. The equilibrium temperature was controlled at $25.0 \pm 0.2\,^\circ C$. For both phases, the densities of the solutions were measured on a densimeter (Type DMA60, Anton Paar). The concentrations of HNO_3 or $UO_2(NO_3)_2$ were titrated. A head space [12] technique was used to determine the partial vapour pressure of the diluent on a gas chromatograph. The water content in the organic phase was determined on a moisture meter (Type CA05, Mitsubishi).

The experimentally studied systems are listed in Table 1. The type of equilibrium (VLE for vapour–liquid equilibrium, VLLE for vapour–liquid–liquid equilibrium) and the number of data points are also given.

CHEMICAL EXTRACTION EQUILIBRIA

The reactions of the extraction of HNO_3 and $UO_2(NO_3)_2$ can be written as

$$H^+ + NO_3^- + TBP_{(0)} = HNO_3 \cdot TBP_{(0)} \tag{1}$$

$$UO_2^{2+} + 2\,NO_3^- + 2\,TBP_{(0)} = UO_2(NO_3)_2 \cdot 2\,TBP_{(0)} \tag{2}$$

TABLE 1

Equilibrium systems studied

No.	System [a]	Equilibrium type [b]	Number of data points
1	n-C_6H_{14}–TBP	VLE	9
2	n-C_7H_{16}–TBP	VLE	9
3	n-C_8H_{18}–TBP	VLE	9
4	n-C_6H_{14}–n-C_7H_{16}–TBP	VLE	36
5	n-C_6H_{14}–n-C_8H_{18}–TBP	VLE	36
6	n-C_7H_{16}–n-C_8H_{18}–TBP	VLE	36
7	H_2O–n-C_7H_{16}–TBP	VLLE	7
8	H_2O–n-C_7H_{16}–HNO_3–TBP (15%)	VLLE	5
9	H_2O–n-C_7H_{16}–HNO_3–TBP (35%)	VLLE	5
10	H_2O–n-C_7H_{16}–HNO_3–TBP (50%)	VLLE	6
11	H_2O–n-C_7H_{16}–HNO_3–TBP (66%)	VLLE	6
12	H_2O–n-C_7H_{16}–HNO_3–TBP (83%)	VLLE	7
13	H_2O–HNO_3–TBP (100%)	VLLE	15
14	H_2O–n-C_7H_{16}–$UO_2(NO_3)_2$–TBP (15%)	VLLE	5
15	H_2O–n-C_7H_{16}–$UO_2(NO_3)_2$–TBP (35%)	VLLE	7
16	H_2O–n-C_7H_{16}–$UO_2(NO_3)_2$–TBP (50%)	VLLE	7
17	H_2O–n-C_7H_{16}–$UO_2(NO_3)_2$–TBP (66%)	VLLE	7
18	H_2O–n-C_7H_{16}–$UO_2(NO_3)_2$–TBP (83%)	VLLE	7
19	H_2O–$UO_2(NO_3)_2$–TBP (100%)	VLLE	7

[a] The percentages in parentheses indicate the initial TBP concentration in vol.%.

[b] VLE denotes vapour–liquid equilibrium; VLLE denotes vapour–liquid–liquid equilibrium.

where the subscript (0) denotes the organic phase. A certain amount of water can also be extracted. According to an NMR study [13], most of the water molecules in the TBP–alkane system exist as discrete physically soluble water. Thus in the organic phase, the possibly existing components are (1) dissolved water, (2) diluent n-C_7H_{16}, (3) extractant TBP, (4) extracted complex $HNO_3 \cdot TBP$, and (5) extracted complex $UO_2(NO_3)_2 \cdot 2$ TBP. The subscripts 1, 2, 3, 4, and 5 will be used to denote these components, respectively.

The thermodynamic equilibrium constants of reactions (1) and (2) are

$$K_H = \frac{a_{HNO_3TBP_{(0)}}}{a_{H^+}a_{NO_3^-}a_{TBP_{(0)}}} = \frac{a_4}{a^2_{+HNO_3}a_3} \tag{3}$$

$$K_U = \frac{a_{UO_2(NO_3)_2 \cdot 2TBP_{(0)}}}{a_{UO_2^{2+}}a_{NO_3^-}a^2_{TBP_{(0)}}} = \frac{a_5}{a^3_{\pm UO_2(NO_3)_2}a_3^2} \tag{4}$$

where a is the thermodynamic activity. For all the components in the organic phase, pure liquid material is taken as the reference state. The concentration is expressed in mole fraction, x, and the relevant activity coefficient is f. For the electrolytes in the aqueous phase, infinite dilution is taken as the reference state and the molal scale is used to express their concentration. Thus eqns. (3) and (4) can be written as

$$K_H = \frac{x_4 f_4}{m_H^2 \gamma_{\pm H}^2 x_3 f_3} \tag{5}$$

$$K_U = \frac{x_5 f_5}{4 m_U^3 \gamma_{\pm U}^3 x_3^2 f_3^2} \tag{6}$$

where the subscripts H and U denote HNO_3 and $UO_2(NO_3)_2$, respectively.

CALCULATION OF THE ACTIVITY COEFFICIENTS

Pitzer's equation will be used to express the activity coefficients of aqueous species, and for all the components in the organic phase, their activity coefficients will be calculated by the UNIFAC method.

Activity coefficients of HNO_3 and $UO_2(NO_3)_2$ in the aqueous phase

According to Pitzer's equation, the mean ionic activity coefficient of the solute in an aqueous solution is expressed as

$$\begin{aligned}\ln \gamma_+ = & -|z_+ z_-| A_\Phi \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right] \\ & + m \frac{2 v_+ v_-}{v} \left\{ 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 I} \left[1 - \left(1 + \alpha I^{1/2} - \tfrac{1}{2}\alpha^2 I \right) \cdot e^{-\alpha I^{1/2}} \right] \right\} \\ & + \tfrac{3}{2} m^2 \left[\frac{2(v_+ v_-)^{3/2}}{v} \right] C^\Phi \end{aligned} \tag{7}$$

where m is the molality concentration of the solute, γ_+ is the mean ionic activity coefficient, z_+ and z_- are the charges of the cation and anion, respectively, $v = v_+ + v_-$ is the total number of ions formed from an electrolyte molecule, $A_\Phi = 0.391$ (at 25 °C), $b = 1.2$, $\alpha = 2.0$, and $I = (\Sigma m_i z_i^2)/2$ is the ionic strength of the solution. For nitric acid, the Pitzer parameters are $\beta^{(0)} = 0.1119$, $\beta^{(1)} = 0.3206$, and $C^\Phi = 0.0010$, while for uranyl nitrate, $\beta^{(0)} = 0.4607$, $\beta^{(1)} = 1.613$, and $C^\Phi = 0.03154$.

Activity of water in the organic phase

In this work, pure water is taken as the reference state for both phases. The activity of water in the electrolyte solution can be calculated by

$$\ln a_w = \frac{M_1 v m}{1000} = -0.018(v m \phi) \tag{8}$$

where M_1 is the molecular weight of water, and ϕ is the osmotic coefficient of the solution, which can be calculated using Pitzer's equation

$$\phi - 1 = -\frac{|z_+ z_-| A_\Phi I^{1/2}}{(1 + bI^{1/2})} + m\frac{2v_+ v_-}{v}\left(\beta^{(0)} + \beta^{(1)}\,\mathrm{e}^{-\alpha I^{1/2}}\right) + m^2\frac{2(v_+ v_-)^{3/2}}{v}C^\Phi \qquad (9)$$

Activity coefficients of organic species using the UNIFAC method

In a multicomponent system, the activity coefficient of component i is composed of two parts

$$\ln f_i = \ln f_i^{\mathrm{c}} + \ln f_i^{\mathrm{R}} \qquad (10)$$

The combinatorial part f_i^{C} represents the contribution from the differences in size and shape of the molecules, and the residual part f_i^{R} from the energy interactions.

The f_i^{c} part can be calculated by

$$\ln f_i^{\mathrm{c}} = \ln\left(\frac{\phi_i}{x_i}\right) + 1 - \frac{\phi_i}{x_i} - \frac{zq_i}{2}\left[\ln\left(\frac{\phi_i}{\theta_i}\right) + 1 - \frac{\phi_i}{\theta_i}\right] \qquad (11)$$

where $z = 10$, is the coordination number, x_i is the mole fraction of component i, ϕ_i its volume fraction, and θ_i its surface area fraction.

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \qquad (12)$$

where r_i is the van der Waals volume and q_i is the van der Waals surface area, and j covers all the components in the system. The values of r_i and q_i can be calculated from the well-defined group volume and surface parameters R_k and Q_k

$$r_i = \sum_k v_k^{(i)} R_k \quad q_i = \sum_k v_k^{(i)} Q_k \qquad (13)$$

Where k is the type of group in the molecule i, and $v_k^{(i)}$ is the number of groups k in a molecule i.

The residual part f_i^{R} can be obtained from the difference of the sums of the activity coefficients of groups in solution and those in the pure component i

$$\ln f_i^{\mathrm{R}} = \sum_k v_{ki}\left(\ln \Gamma_k - \ln \Gamma_k^{(i)}\right) \qquad (14)$$

where Γ_k is the residual activity coefficient of group k in the solution and $\Gamma_k^{(i)}$ is that in pure component i. The group activity coefficient Γ_k is calculated by

$$\ln \Gamma_k = Q_k\left[1 - \ln\left(\sum_m \Theta_m \psi_{mk}\right) - \sum_m\left(\Theta_m \psi_{km} / \sum_n \Theta_n \psi_{nm}\right)\right] \qquad (15)$$

Where Θ_m is the surface area fraction of group m in the whole solution

$$\Theta_m = \frac{\left(Q_m \sum_j x_j v_m^{(j)}\right)}{\sum_n \left(Q_n \sum_j x_j v_n^{(j)}\right)} \tag{16}$$

and ψ_{nm} is the Boltzmann factor relevant to the interaction parameter between groups n and m

$$\psi_{nm} = \exp\left(\frac{-a_{nm}}{T}\right) \tag{17}$$

Derivation of the experimental activity coefficients in the organic phase

The diluent

At 1 atm and 25 ° C, the vapour of a diluent can be treated as an ideal gas. Its fugacity can be replaced by its partial pressure p_i, which is proportional to its peak area A_i on the gas chromatogram. Thus the activity coefficient is obtained by

$$a_i = \frac{p_i}{p_i^0} = \frac{A_i}{A_i^0} \tag{18}$$

and the activity coefficient is then

$$f_i = \frac{a_i}{x_i} = \frac{A_i}{A_i^0 x_i} \tag{19}$$

where p_i^0 and A_i^0 are the partial pressure and the peak area of pure diluent i.

TBP

For binary and ternary TBP–alkane systems, after the above activity coefficient(s) has been obtained, the activity coefficient of TBP can easily be derived according to the Gibbs–Duhem equation

$$\sum_i x_i \, \mathrm{d} \ln f_i = 0 \tag{20}$$

$$\ln f_i = -\frac{1}{x_i} \sum_{j \neq i} \int_{x_i=1}^{x_i} x_j \, \mathrm{d} \ln f_j \tag{21}$$

Water

Based on the equality of the chemical potentials of water between the aqueous phase and the organic phase, the activity of water in the organic phase can be obtained by

$$a_1 = a_{\mathrm{w}} \tag{22}$$

The value of a_w has been given in equation (8). Then we have

$$f_1 = \frac{a_1}{x_1} = \frac{a_w}{x_1} \tag{23}$$

RESULTS AND DISCUSSION

Group assignment

The volume and surface parameters R_k and Q_k for commonly found groups, i.e. CH_3, CH_2, OCH_2, and H_2O, are well-defined by Fredenslund and co-workers [14,15]. Rozen and Prausnitz divided the TBP molecule into groups of CH_3, CH_2, OCH_2 and PO [11]. In this work, this assignment is followed.

The group division of the extracted complex $HNO_3 \cdot TBP$ and $UO_2(NO_3)_2 \cdot 2TBP$ has not yet been found in the literature. To facilitate the calculation as well as to better express the interaction among the groups, we will take $POHNO_3$ or $(PO)_2UO_2(NO_3)_2$ (abbreviated as UONP) as one single group. For $POHNO_3$, the R_k and Q_k values can be obtained by summing those of groups PO, OH and NO_3 [7,16]. For UONP, R_k is estimated from the ratio of the mole volume of TBP (273.7 ml mol^{-1}) to that of $UO_2(NO_3)_2 \cdot 2TBP$ (623 ml mol^{-1}). The group assignment of n-C_7H_{16}, TBP, $HNO_3 \cdot TBP$, and $UO_2(NO_3)_2 \cdot 2TBP$ is shown in Table 2. The R_k and Q_k values are listed in Table 3.

TABLE 2

Group assignment examples

Compound	Group number, υ_k					
	CH_3	CH_2	OCH_2	PO	$POHNO_3$	UONP [a]
n-C_7H_{16}	2	5	0	0	0	0
TBP	3	6	3	1	0	0
$HNO_3 \cdot TBP$	3	6	3	0	1	0
$UO_2(NO_3)_2 \cdot 2TBP$	6	12	6	0	0	1

[a] Denotes the group $UO_2(NO_3)_2(PO)_2$.

TABLE 3

The volume parameter R_k and the surface area parameter Q_k of the groups

	Group						
	CH_3	CH_2	OCH_2	H_2O	PO	HNO_3PO	UONP
R_k	0.9011	0.6744	0.9183	0.92	0.97	2.606	4.833
Q_k	0.848	0.540	0.78	1.40	0.876	2.48	5.0

Estimation of group-interaction parameters

Part of systems are regressed on computer for obtaining the group-interaction parameters, and others for the test of the precision of prediction. All the parameters except for CH_2–OCH_2 are estimated. The system regressed and the object function F used in this procedure are as follows.

(a) Three binary systems (systems 1–3 in Table 1), 27 experimental points in total

$$F = \sum_{p=1}^{27} \sum_{i=1}^{2} |f_{i(\mathrm{cal})} - f_{i(\mathrm{exp})}|_p \tag{24}$$

where the subscript (cal) denotes values calculated using UNIFAC, and (exp) the experimental values according to eqn. (19) for the diluent, and eqn. (21) for TBP.

(b) Solubility of water in the organic phase (system 7 in Table 1), 7 points

$$F = \sum_{p=1}^{7} |x_{1(\mathrm{cal})} - x_{1(\mathrm{exp})}|_p \tag{25}$$

$x_{1(\mathrm{cal})}$ is given by eqn. (23).

(c) Extraction of HNO_3 by n-C_7H_{16}–TBP, (systems 9 and 12 in Table 1), 12 points in total

$$F = \sum_{p=1}^{12} \{ |x_{1(\mathrm{cal})} - x_{1(\mathrm{exp})}| + |x_{4(\mathrm{cal})} - x_{4(\mathrm{exp})}| \}_p \tag{26}$$

$$x_{4(\mathrm{cal})} = K_{\mathrm{H}} m_{\mathrm{H}}^2 \gamma_{\pm \mathrm{H}}^2 x_3 \frac{f_3}{f_4} \tag{27}$$

(d) Extraction of $UO_2(NO_3)_2$ by n-C_7H_{16}–TBP (systems 15 and 18 in Table 1), 14 points in total

$$F = \sum_{p=1}^{14} \{ |x_{1(\mathrm{cal})} - x_{1(\mathrm{exp})}| + |x_{5(\mathrm{cal})} - x_{5(\mathrm{exp})}| \}_p \tag{28}$$

$$x_{5(\mathrm{cal})} = 4K_{\mathrm{U}} m_{\mathrm{U}}^3 \gamma_{\pm \mathrm{U}}^3 x_3^2 \frac{f_3^2}{f_4} \tag{29}$$

The obtained group-interaction parameters are shown in Table 4.

Prediction of liquid–liquid equilibria

Now that we have the group-interaction parameter a_{mn} values, we can calculate the activity coefficients of the components, and predict the equi-

TABLE 4

Group-interaction parameter values a_{mn} used in this work

n	a_{mn}					
	$m = CH_3$	OCH_2	PO	H_2O	HNO_3PO	UONP
CH_3	0.000	251.5	2694.0	1278.0	945.1	847.2
OCH_2	83.36	0.000	−422.3	−52.64	−648.7	−655.6
PO	442.5	304.0	0.000	4388.0	37.25	812.8
H_2O	804.8	−61.78	−569.7	0.000	6582.0	6225.0
HNO_3PO	−1173.0	−730.3	−633.8	−1519.0	0.000	
UONP	−1862.0	−1439.0	−392.4	3091.0		0.000

librium compositions. This can be done by solving the simultaneous equations

$$\begin{aligned} & x_1 + x_2 + x_3 + x_4 + x_5 = 1 \\ & x_1 f_1 = a_w \\ & \frac{x_3 + x_4 + 2x_5}{x} = \text{const.} \\ & K_H = \frac{x_4 f_4}{m_H^2 \gamma_{\pm H}^2 x_3 f_3} \\ & K_U = \frac{x_5 f_5}{4 m_U^3 \gamma_{\pm U}^3 x_3^2 f_3^2} \end{aligned} \qquad (30)$$

Deviations of the calculated compositions of the organic phase from the experimentally obtained ones are given in Table 5–7. Results show that the UNIFAC method can be used for the correlation and prediction of TBP extraction systems with satisfactory precision. Using the group-interaction

TABLE 5

Deviations of correlation for vapour–liquid systems

System	δf_1 [a]	δf_2 [a]	δf_3 [a]
	(%)		
n-C_6H_{14} (1)–TBP (2)	1.9	1.3	
n-C_7H_{16} (1)–TBP (2)	2.3	1.0	
n-C_8H_{18} (1)–TBP (2)	2.5	1.9	
n-C_6H_{14} (1)–n-C_7H_{16} (2)–TBP (3)	3.2	4.3	4.1
n-C_6H_{14} (1)–n-C_8H_{18} (2)–TBP (3)	1.7	3.9	4.0
n-C_7H_{16} (1)–n-C_8H_{18} (2)–TBP (3)	2.1	4.1	3.4

[a] The average relative deviation for the activity coefficient

$$\delta f_i = \frac{\sum^{n} |(f_{i(c)}/f_{i(e)}) - 1.0|}{n} \times 100\%$$

TABLE 6

Deviations of correlation for H_2O–n-C_7H_{16}–TBP extraction systems

System [a] (organic phase only)	Δx_1 [b]	Δx_4 [b]
H_2O (1)–n-C_7H_{16} (2)–TBP (3)	0.011	
H_2O (1)–n-C_7H_{16} (2)–TBP (3) (15%)–HNO_3·TBP (4)	0.007	0.001
H_2O (1)–n-C_7H_{16} (2)–TBP (3) (35%)–HNO_3·TBP (4)	0.009	0.003
H_2O (1)–n-C_7H_{16} (2)–TBP (3) (50%)–HNO_3·TBP (4)	0.010	0.004
H_2O (1)–n-C_7H_{16} (2)–TBP (3) (66%)–HNO_3·TBP (4)	0.006	0.003
H_2O (1)–n-C_7H_{16} (2)–TBP (3) (83%)–HNO_3·TBP (4)	0.016	0.003
H_2O (1)–TBP (3) (100%)–HNO_3·TBP (4)	0.014	0.004

[a] Percentages indicate the initial TBP concentration of the extraction system.

[b] The average deviation of the concentration in mole fraction

$$\Delta x_i = \frac{\sum^{n} | x_{i(c)} - x_{i(e)} |}{n}$$

TABLE 7

Deviation of correlation for H_2O–n-C_7H_{16}–$UO_2(NO_3)_2$–TBP extraction systems

System [a]	Δx_1 [b]	Δx_5 [b]
H_2O (1)–n-C_7H_{16} (2)–TBP (15%) (3)–$UO_2(NO_3)_2$·2TBP (5)	0.015	0.002
H_2O (1)–n-C_7H_{16} (2)–TBP (35%) (3)–$UO_2(NO_3)_2$·2TBP (5)	0.018	0.002
H_2O (1)–n-C_7H_{16} (2)–TBP (50%) (3)–$UO_2(NO_3)_2$·2TBP (5)	0.020	0.003
H_2O (1)–n-C_7H_{16} (2)–TBP (66%) (3)–$UO_2(NO_3)_2$·2TBP (5)	0.027	0.003
H_2O (1)–n-C_7H_{16} (2)–TBP (83%) (3)–$UO_2(NO_3)_2$·2TBP (5)	0.022	0.003
H_2O (1)–TBP (100%) (3)–$UO_2(NO_3)_2$·2TBP (5)	0.025	0.006

[a] Percentages indicate the initial TBP concentration of the extraction system.

[b] The average deviation of the concentration in mole fraction

$$\Delta x_i = \frac{\sum^{n} | x_{i(c)} - x_{i(e)} |}{n}$$

TABLE 8

Comparison of predicted concentrations with experimental results for the system H_2O–n-C_7H_{16}–TBP (initial 66 vol.%)–HNO_3 at 25°C and 1 atm. [a]

m	γ_+	a_4	$x_{1(e)}$	$x_{2(e)}$	$x_{3(e)}$	$x_{4(e)}$	$x_{1(c)}$	$x_{4(c)}$
0.0936	0.7915	0.9968	0.2912	0.3479	0.3589	0.0019	0.2824	0.0022
0.3680	0.7253	0.9876	0.2854	0.3608	0.3418	0.0220	0.2752	0.0212
0.7345	0.7142	0.9749	0.2714	0.3563	0.3127	0.0569	0.2659	0.0536
1.3300	0.7371	0.9531	0.2594	0.3636	0.2650	0.1121	0.2511	0.1038
3.4330	0.9678	0.8624	0.2084	0.3886	0.1440	0.2590	0.2019	0.2538
5.1040	1.2933	0.7765	0.1640	0.4104	0.0769	0.3487	0.1640	0.3487

[a] Subscripts: (e) denotes experimental results and (c) denotes calculated values.

TABLE 9

Comparison of predicted concentrations with experimental results for the system H_2O–*n*-C_7H_{16}–TBP (initial 66 vol.%)–$UO_2(NO_3)_2$ at 25 °C and 1 atm.[a]

m	γ_+	a_1	$x_{1(e)}$	$x_{2(e)}$	$x_{3(e)}$	$x_{5(e)}$	$x_{1(c)}$	$x_{5(c)}$
0.0121	0.7138	0.9994	0.2706	0.3581	0.3711	0.0001	0.2854	0.0004
0.0595	0.5760	0.9972	0.2593	0.3671	0.3664	0.0072	0.2748	0.0142
0.1489	0.5199	0.9929	0.2019	0.4179	0.3270	0.0532	0.2242	0.0583
0.2296	0.5079	0.9888	0.1592	0.4599	0.2848	0.0961	0.1903	0.0993
0.2923	0.5076	0.9855	0.1348	0.4888	0.2459	0.1305	0.1678	0.1293
0.3939	0.5161	0.9798	0.1105	0.5195	0.2012	0.1688	0.1459	0.1688
0.4980	0.5325	0.9736	0.0942	0.5401	0.1713	0.1944	0.1325	0.2001

[a] Subscripts: (e) denotes experimental results and (c) denotes calculated values.

parameters drawn from systems with initial TBP concentration of 35 and 83 vol.%, the mole fractions of water, $HNO_3 \cdot TBP$ or $UO_2(NO_3)_2 \cdot 2TBP$ for all the systems with other initial TBP concentrations are obtained. Expressed in mole fraction, the average absolute derivation of $HNO_3 \cdot TBP$ or $UO_2(NO_3)_2 \cdot 2TBP$ is 0.003, and that of water is 0.011 for the system extracting HNO_3 and 0.021 for the system extracting $UO_2(NO_3)_2$.

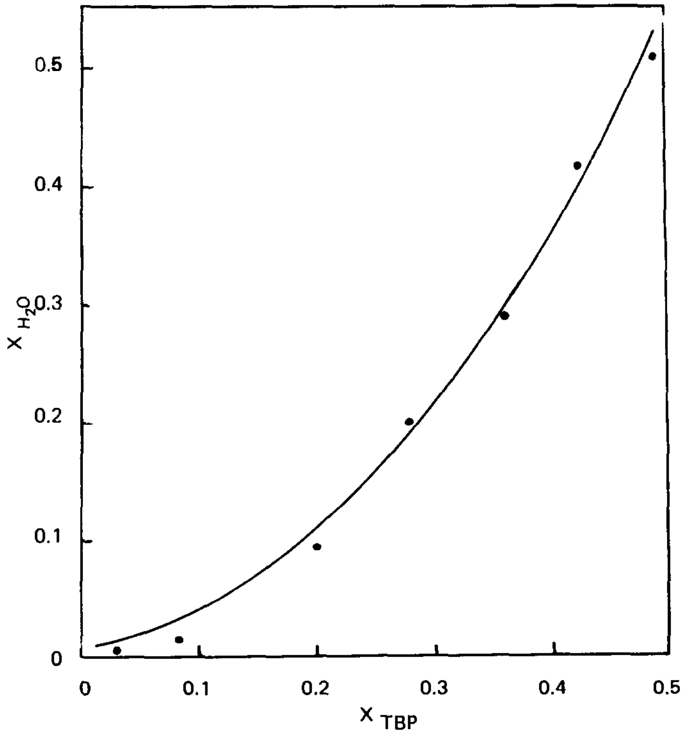

Fig. 1. Solubility of water in the organic phase. System $H_2O(1)$–*n*-$C_7H_{16}(2)$–TBP(3) at 25 °C and 1 atm. ●, Experimental results; ———, calculated values.

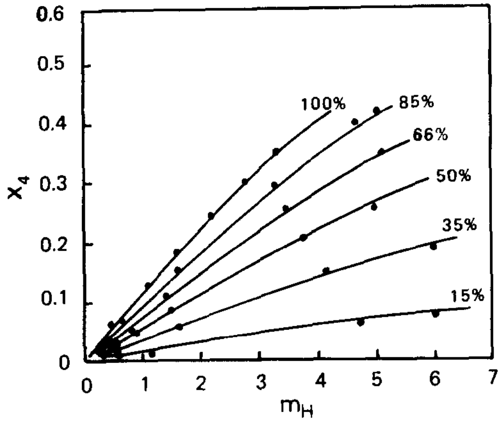

Fig. 2. Partition isotherms of HNO_3 between the aqueous phase and the organic phase. System H_2O–n-C_7H_{16}–TBP–HNO_3 at 25 °C and 1 atm. x_4 is the mole fraction of $HNO_3 \cdot$ TBP in the organic phase, m_H is the molality concentration of HNO_3 in the aqueous phase.

As an example, the results of the systems with an initial TBP concentration of 66 vol.% are given in Tables 8 and 9, in which (e) denotes the experimental and (c) the calculated values. Figure 1 shows the physical extraction of water with n-C_7H_{16}–TBP. Figures 2 and 3 show the extraction of HNO_3 and $UO_2(NO_3)_2$ with n-C_7H_{16}–TBP. The percentages on the curves are the initial TBP concentrations by volume. In these figures, the solid lines are the calculated values using the UNIFAC equations, and the points are the experimental results. In the chemical extraction systems, the

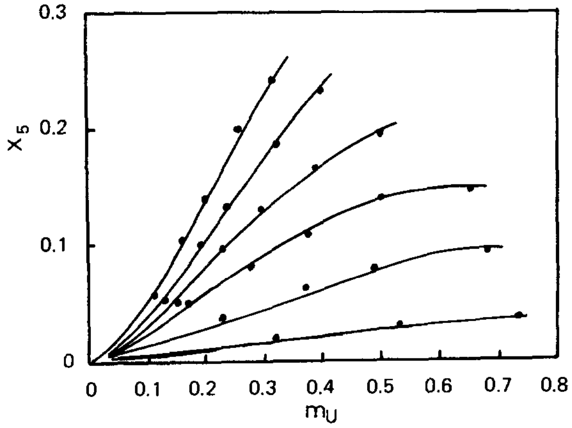

Fig. 3. Partition isotherms of $UO_2(NO_3)_2$ between the aqueous phase and the organic phase. System H_2O–n-C_7H_{16}–TBP–$UO_2(NO_3)_2$ at 25 °C and 1 atm. x_5 is the mole fraction of $UO_2(NO_3)_2 \cdot 2TBP$ in the organic phase, m_U is the molality concentration of $UO_2(NO_3)_2$ in the aqueous phase.

equilibrium concentration of HNO_3 in the aqueous phase can be as high as 7 m, and the concentration of $UO_2(NO_3)_2$ is up to 0.8 m. This gives us the confidence to use the UNIFAC method for practical TBP extraction systems.

SYMBOLS

a	thermodynamic activity
a_{nm}	group-interaction parameter between group n and m in the UNIFAC equation
A	peak area of a component in the gas chromatogram
A_ϕ	constant in the Pitzer equation (0.391 at 25 °C)
b	constant in the Pitzer equation (equal to 1.2)
C^Φ	Pitzer's parameter [0.0010 for HNO_3 and 0.03154 for $UO_2(NO_3)_2$]
f	activity coefficient of a component in the organic phase
K_H	equilibrium constant of the extraction of HNO_3 by TBP
K_U	equilibrium constant of the extraction of $UO_2(NO_3)_2$ by TBP
m	molality concentration of a solute in the aqueous phase
p	partial vapour pressure of a diluent above the solution
q_i	van der Waals surface area of component i
Q_k	surface area parameter of group k in the UNIFAC equation
r_i	van der Waals volume of component i
R_k	volume parameter of group k in the UNIFAC equation
T	absolute temperature
x	mole fraction of a component in the organic phase
z	charge number of an aqueous species
α	constant in Pitzer's equation (equal to 2.0)
$\beta^{(0)}$	Pitzer's parameter [0.1119 for HNO_3 and 0.4607 for $UO_2(NO_3)_2$]
$\beta^{(1)}$	Pitzer's parameter [0.3206 for HNO_3 and 1.613 for $UO_2(NO_3)_2$]
γ_+	mean ionic activity coefficient of a solute in the aqueous phase
Γ_k	activity coefficient of group k in the UNIFAC equation
θ_i	surface area fraction of component i in a mixture
θ_k	surface area fraction of group k
ϕ	osmotic coefficient of an aqueous solution
ϕ_i	volume fraction of component i in a mixture

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