



Modelling of uranyl nitrate and nitric acid extraction in diluted TBP using Chem-UNIFAC
 M. Hanna, B. Rat (CEA : DCC/DRRV/SEMP/LMP ValRhô Marcoule, bat. 166, B.P. 17171, 30207
 Bagnols-sur-Cèze, France)

ABSTRACT

Chem-UNIFAC model is applied to TBP/dodecane/water/ $\text{UO}_2(\text{NO}_3)_2$ and TBP/dodecane/water/ HNO_3 systems, following our previous studies on TBP/diluent (alkane, HCCl_3 , CCl_4) and TBP/diluent/water/salting out agent (same diluents) systems. New Chem-UNIFAC parameters for TBP/water pair are calculated and an unique set of parameters is proposed to describe the TBP/dodecane/water/ $\text{UO}_2(\text{NO}_3)_2$ system, for a wide range of TBP/diluent volume proportions (10%, 30%, 50%, 100%) and a wide range of uranyl nitrate aqueous concentration. Nitric acid and water extraction in TBP/dodecane/water/ HNO_3 is also calculated and an improvement is found in the description of the corresponding isotherms.

INTRODUCTION

The present work is the continuation of our previous studies (1) on the application of UNIQUAC and UNIFAC equations to correlate thermodynamic properties of organic phase in metal solvent extraction.

The two main features of UNIQUAC and UNIFAC equations in estimating thermodynamic properties of organic phase in metal solvent extraction, are to take into account extractant percentage and diluent influence, and to use only binary parameters to describe multicomponent systems. The further advantage of UNIFAC equation lies in group contribution which gives it a more important predictive power.

In the later studies, UNIQUAC interaction parameters, regressed on TBP/diluent (alkane, CCl_4 , HCCl_3) mixtures, already permitted to calculate both activity coefficients and enthalpies of mixing. UNIFAC, using group contribution, allowed to represent different TBP/n-alkane mixtures with only two interaction parameters, but made no distinction between branched alkanes. We used the interaction parameters regressed on binary system TBP/diluent and TBP/ H_2O to estimate the solubility of water in TBP/diluent mixtures as a function of water activity and TBP percentage. For a correct description of TBP/diluent/ $\text{H}_2\text{O}/\text{LiCl}$ system, it was necessary, except in case of alkane, to supplement UNIFAC equation by explicitly taking into account formation of complexes (Chem-UNIFAC). This work allowed to improve the representation of these systems (2,3,4).

We present here our last results on TBP/dodecane/water/electrolyte systems with uranyl nitrate and nitric acid. Extraction isotherm of both electrolytes were described with a good precision, for a wide range of concentration of both species in water and a wide range of TBP/diluent proportions. Furthermore Chem-UNIFAC parameters ^a for (TBP, H_2O) pair were re-fitted on TBP/dodecane/water/ $\text{UO}_2(\text{NO}_3)_2$ system, in order to better take into account the proportion of water extracted as a $\text{TBP} \cdot \text{H}_2\text{O}$ complex.

UNIQUAC AND UNIFAC MODELS

For a multicomponent system, the UNIQUAC equation for the molar excess Gibbs energy is composed of two parts (5,6) : the combinatorial part, essentially due to differences in size and shape of the molecules, and a residual contribution, essentially due to energetic interactions.

$$\frac{g^E}{RT} = \begin{cases} \frac{g_{\text{combinatorial}}^E}{RT} = \sum_i x_i \ln \frac{\phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\phi_i} \\ \frac{g_{\text{residual}}^E}{RT} = -\sum_i q_i x_i \ln \left(\sum_i \theta_i \exp \left(-\frac{a_{ji}}{T} \right) \right) \end{cases} \quad \text{Eq. 1}$$

where :

^a we refer here (and afterwards) to the set of interaction parameters ($a_{\text{H}_2\text{O},\text{TBP}}$; $a_{\text{TBP},\text{H}_2\text{O}}$) associated to equilibrium constant of $\text{TBP} \cdot \text{H}_2\text{O}$ complex.

q_i is the area parameter of component i , ϕ_i and θ_i are the volume and area fractions of component i , a_{ji} is the interaction parameter between molecule i and j

UNIFAC model adopts the same formalism as UNIQUAC model but introduces the group contribution concept, *i. e.* molecules are considered as structural group assemblies. The UNIFAC method being based on the group contribution concept has the advantage that it can be used in the calculation of multicomponent system with a small number of parameters. The Chem-UNIFAC model explicitly allows for the formation of A.B complexes considering the equilibrium constant of formation of the later :

$$K_{A,B} = \frac{X_{A,B} \gamma_{A,B}}{X_A \gamma_A X_B \gamma_B} \quad \text{Eq. 2}$$

where the activity coefficients are calculated with the UNIFAC model.

TBP/dodecane/ $\text{UO}_2(\text{NO}_3)_2$ /water mixtures

Some authors (7,8) were already interested in UNIQUAC and UNIFAC models to evaluate non-ideality of such organic phases. But none of them took water extraction into consideration or considered it to be negligible.

In the following, Chem-UNIFAC model is used. Water extraction is explicitly taken into account and the formation of a $\text{TBP} \cdot \text{H}_2\text{O}$ complex and a $2\text{TBP} \cdot \text{UO}_2(\text{NO}_3)_2$ complex are considered. Uranyl nitrate and water activity coefficients are calculated and compared to experimental data (see Figure 1) (9). An unique set of Chem-UNIFAC parameter (interaction parameter and equilibrium constant : see Table 1) is found to describe the entire range of TBP/diluent proportion (10% vol., 30% vol., 50% vol., 100% vol.), within an excellent agreement between experimental and calculated data.

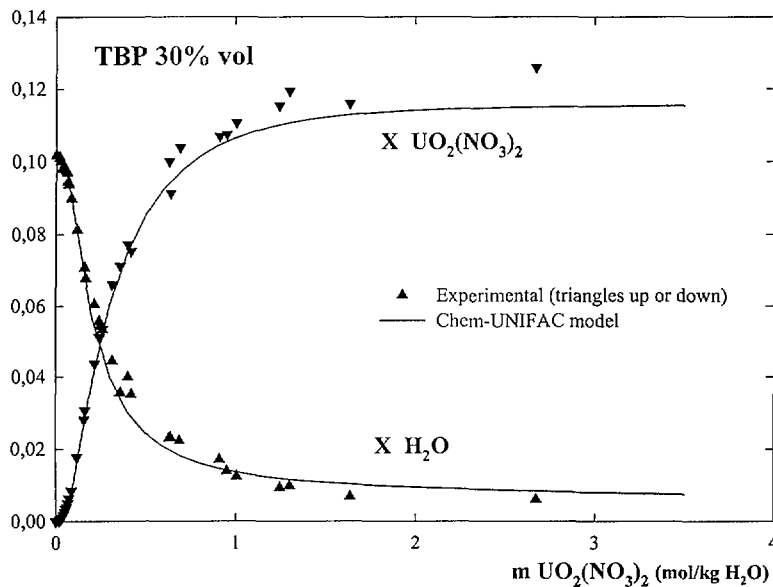


Figure 1 : TBP and $\text{UO}_2(\text{NO}_3)_2$ concentration in TBP/dodecane/ $\text{UO}_2(\text{NO}_3)_2$ /water mixtures

Table 1 : Chem-UNIFAC parameters for TBP/dodecane/ $\text{UO}_2(\text{NO}_3)_2$ /water system

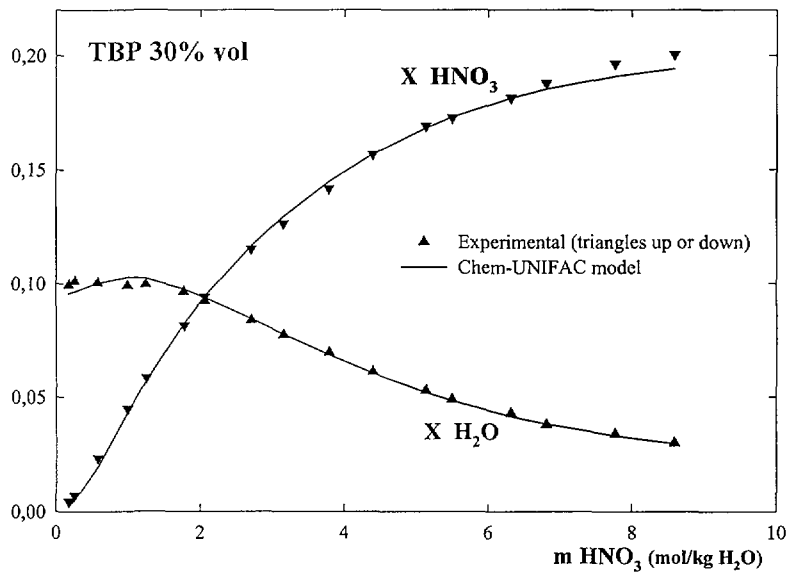
$a_{nm}(K)$	H_2O	dodecane	TBP	$\text{UO}_2(\text{NO}_3)_2$
H_2O	0	89.6	$3e+6$	$2e+33$
dodecane	1922	0	40	-110
TBP	532	30	0	-143
$\text{UO}_2(\text{NO}_3)_2$	$5e+7$	-282	-227	0

Equilibrium constants :

$$2\text{TBP} + \text{UO}_2(\text{NO}_3)_2 \rightleftharpoons \overline{2\text{TBP}.\text{UO}_2(\text{NO}_3)_2} \quad K_{T_{2\text{TBP}.\text{UO}_2(\text{NO}_3)_2}} = 57$$

$$\text{TBP} + \text{H}_2\text{O} \rightleftharpoons \overline{\text{TBP}.\text{H}_2\text{O}} \quad K_{T_{\text{TBP}.\text{H}_2\text{O}}} = 1.2$$
TBP/dodecane/ HNO_3 /water mixtures

No previous theoretical job was done on this system using UNIQUAC/UNIFAC models but experimental data were available (10). Chem-UNIFAC model is applied, water extraction is explicitly calculated and taken into account through the formation of a $\text{TBP}.\text{H}_2\text{O}$ complex. $\text{TBP}.\text{HNO}_3$ and $2\text{TBP}.\text{H}_2\text{O}.\text{HNO}_3$ complexes are considered. Nitric acid and water activity coefficients are calculated and mole fraction of each species are compared to experimental data (Figure 2 and Table 2) (9).

**Figure 2 : TBP and HNO_3 concentration in TBP/dodecane/ HNO_3 /water mixtures****Table 2 : Chem-UNIFAC parameters for TBP/dodecane/ HNO_3 /water mixtures**

$a_{nm}(K)$	H_2O	dodecane	TBP	HNO_3
H_2O	0	89.6	$3e+6$	-259
dodecane	1922	0	40	119
TBP	532	30	0	53
HNO_3	-34	161	-13	0

Equilibrium constants :

$$\text{TBP} + \text{HNO}_3 \rightleftharpoons \overline{\text{TBP}.\text{HNO}_3} \quad K_{T_{\text{TBP}.\text{HNO}_3}} = 0.74$$

$$2\text{TBP} + \text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \overline{2\text{TBP}.\text{H}_2\text{O}.\text{HNO}_3} \quad K_{T_{2\text{TBP}.\text{H}_2\text{O}.\text{HNO}_3}} = 5.9$$

$$\text{TBP} + \text{H}_2\text{O} \rightleftharpoons \overline{\text{TBP}.\text{H}_2\text{O}} \quad K_{T_{\text{TBP}.\text{H}_2\text{O}}} = 1.2$$

DISCUSSION

Chem-UNIFAC parameters for (TBP, H₂O) pair^b were previously calculated (1) using TBP/water/salting out agent experimental data. The latter led to mere description of TBP/dodecane/UO₂(NO₃)₂/water and TBP/dodecane/HNO₃/water experimental data. They were therefore re-fitted on TBP/dodecane/UO₂(NO₃)₂/water system and the found parameters led to a good description of corresponding extraction isotherms and to improve afterwards our previous description of TBP/dodecane/HNO₃/water extraction experimental data. This stage allowed to improve our understanding of the proportion of water extracted in the organic phase through solubilization and the proportion extracted through complexation. Indeed, no experimental data is available for TBP/water/salting out agent allowing to determine this proportion. Furthermore, in TBP/dodecane/HNO₃/water, the presence of the 2TBP.water.HNO₃ complex makes it very difficult to determine an unique set of parameter corresponding to that repartition. The study of TBP/dodecane/UO₂(NO₃)₂/water led us to think that the part of water complexed in TBP is greater than we thought previously (K_{TBP,H_2O} increased from 0.1 to 1.2).

This modification is assigned to two combined features. Distribution coefficient of uranyl nitrate is very high, which means that a great and increasing part of TBP is complexed with uranyl nitrate along the isotherm. Since organic phase water concentration strongly decreases at the same time, we think that a great part of the water is in the complexed form at the beginning of the isotherm. So we think the (TBP, H₂O) Chem-UNIFAC parameters describe at the best the cited proportion of the water solubilized and the complexed one.

Furthermore, it has been shown (11) that, fitting of UNIFAC/UNIQUAC interaction parameters with liquid-liquid or liquid-vapour equilibrium experimental data, cannot lead to an unique set of parameters, due to correlation between parameters. This was also observed during our calculations. The last calculations allowed to discriminate between several pairs of interaction parameters.

CONCLUSION

TBP/dodecane/UO₂(NO₃)₂/water and TBP/dodecane/HNO₃/water extraction isotherms have been successfully described with Chem-UNIFAC equation. Furthermore an indeterminacy on the proportion of solubilized and complexed water in these systems, due to lack of experimental evidence, has been overcome. This study improved our willingness to look for a microscopic interpretation of the interaction between water and TBP and its translation to UNIFAC interaction parameters. Therefore, our next step will be to calculate UNIFAC interaction parameters for TBP/alcane/water system with molecular mechanics methods (11), in order to have a general view of the application of UNIFAC models to metal ion extraction.

-
- 1 B. Rat, : Ph. D. thesis, Université Paris VI (1998)
 - 2 J. Li, Y. Li, J. Chen, J. Lu and T. Teng, *Fluid Phase Equilibria*, **58**, 307-318 (1990)
 - 3 A. M. Rozen, V. G. Yurkin, Y. V. Kononov, M. P. Shapovalov and B. V. Krupnov, *Russ. J. Phys. Chem*, **69**, 2, 225-234 (1995)
 - 4 A. K. Pyartman and A. A. Kopyrin, *Radiochemistry*, **38**, 2, 154-156 (1996)
 - 5 J. M. Prausnitz, R. N. Lichtenthaler and E. G. d. Azevedo, *Molecular Thermodynamics of Fluid Phase Equilibria*, Englewood Cliffs ed., Prentice-Hall, NJ (1986)
 - 6 A. Fredenslund, J. Gmehling and P. Rasmussen, *Vapor-Liquid Equilibria using UNIFAC, a Group Contribution Method*, Elsevier Scientific Publishing Company (1977)
 - 7 Z. Li, J. Chen, T. Bao, Y. Shang and Y. Li, *Thermochimica Acta*, **169**, 287-300 (1990)
 - 8 J. Chen, Z. Li, J. Lu and Y. Li, *Fluid Phase Equilibria*, **81**, 1-15 (1992)
 - 9 C. Sorel : Private communication
 - 10 B. Mokili :Ph. D. thesis, University Paris VI (1992)
 - 11 S. O. Jonsdottir, K. Rasmussen, A. Fredenslund, *Fluid Phase Equilibria*, **100**, p 121 (1994)

^b interaction parameters ($a_{H_2O,TBP}$, a_{TBP,H_2O}) associated to equilibrium constant of TBP.H₂O complex.