



## **NEW APPROACH FOR THIRD PHASE INVESTIGATION IN SOLVENT EXTRACTION SYSTEM**

Marian BORKOWSKI

Los Alamos National Laboratory, Carlsbad Operations, NM 88220, USA  
e-mail: [marian@lanl.gov](mailto:marian@lanl.gov)

---

### **ABSTRACT**

The phenomenon of third phase formation in different liquid extraction systems is well known for more than 50 years but until now a good mathematical model that could predict the third phase formation has not been developed. The third phase is unwanted in extraction systems because, for example, in nuclear fuel reprocessing it can cause criticality problems. However, the third phase may be a useful tool in other technologies. In this paper a new approach to third phase investigation is proposed. This new approach eliminates the aqueous phase, simplifies the system and gives new insight in the nature the third phase. It is a step forward in understanding of the mechanism governing the formation of third phase. This new approach could quickly provide sufficient data to develop a comprehensive model.

Keywords: Third phase / TBP / Nitric acid / Dodecane / Solvent extraction

---

### **INTRODUCTION**

When a solution of tri-n-butyl phosphate (TBP) in an aliphatic hydrocarbon diluent is loaded with tetravalent, or hexavalent metal ions and/or a mineral acid, the formation of a heavy and a light organic phase is often observed. The heavy organic phase (HOP) contains mostly of the extractant, metal and acid, and the light organic phase (LOP) is rich in diluent and contains much less of the extractant, metal and acid. Third phase formation in solvent extraction is a well known phenomenon and has been investigated for a number of systems [1–4]. The majority of these studies have focused on the conditions under which third phase formation appears and ways of avoiding its formation. The results of these investigations have been reviewed in two major works [5, 6]. In general, third phase formation has been attributed to the limited solubility of the metal-ligand complex in the non-polar organic phase. However, a quantitative understanding of this phenomenon has not been formulated. The Flory–Huggins theory of polymer

solutions was applied for the interpretation and theoretical prediction of third phase formation in the extraction of  $\text{HNO}_3$  by a substituted malonamide in dodecane [7]. Recently, the importance of third phase formation has expanded beyond spent nuclear fuel reprocessing. In the last few years TBP third phases have been used for the preparation of ultrafine  $\text{TiO}_2$  and  $\text{ZrO}_2$  powders with small grain sizes and within a narrow distribution. [8, 9] Third phase formation was also used as a method for extractant purification [10].

The extraction of nitric acid by TBP has been widely investigated and the results are collected in a book chapter [11]. Third phases are observed when solutions of TBP in kerosene or dodecane are equilibrated with nitric acid and the aqueous equilibrium concentration of acid is higher than 14 M. The  $\text{HNO}_3$  to TBP molar ratio in the HOP varies between 1.18 and 1.92, indicating the formation of species with the stoichiometry  $\text{TBP}\cdot 2\text{HNO}_3$  (hemisolvate) and, possibly, of other species such as  $\text{TBP}\cdot 3\text{HNO}_3$  and  $\text{TBP}\cdot 4\text{HNO}_3$  [12]. When the aliphatic diluent has a shorter chain, the solubility of the complex increases and third phase formation is less likely, e.g., concentrated nitric acid (16 M) does not form a third phase with TBP solution in *n*-octane. Third phase formation is more frequently encountered in the presence of metal salts. For 20% TBP in *n*-dodecane, the presence of 1 M  $\text{UO}_2(\text{NO}_3)_2$  in the aqueous phase decreases the concentration of nitric acid necessary for third phase formation to 9 M. The presence of a thorium salt decreases the lower limit of nitric acid concentration necessary for third phase formation even more significantly than uranium salts. Although analytical data for these systems have been reported [2, 3, 12, 13], little structural information is available. In the previous study, [14] the infrared spectra of nitric acid in solutions of tri-*n*-butyl phosphate in *n*-octane have been interpreted, and a method for differentiating between weakly intermolecularly hydrogen-bonded and strongly bonded nitric acid present in the organic phase has been developed. The structural analysis of nitric acid in third phases formed by solutions of TBP in *n*-dodecane or *n*-octane in the presence of  $\text{UO}_2(\text{NO}_3)_2$ ,  $\text{Zr}(\text{NO}_3)_4$  and  $\text{Th}(\text{NO}_3)_4$  was studied using small angle neutron scattering (SANS) [15-22].

In this work a new approach for third phase investigation is presented. This approach eliminates the aqueous phase in the third phase generation shedding a new light on the nature of third phase. The present work is a step forward in understanding the mechanism governing the formation of third phase.

## RESULTS AND DISCUSSION

The typical approach for third phase investigation is determination of the Limit of Organic Concentration (LOC), which is the highest concentration of metal, acid or their sum in the organic phase for which only

one organic phase is observed. Small additions of metal or acid to the organic phase result in the organic phase splitting. In Figure 1 the dependence of thorium extraction from 5 M nitric acid using 20% TBP in *n*-octane is presented. Such systems are usually characterized by measurements of the extracted specie's concentrations (the *y*-variable) as a function of component concentrations in the aqueous phase (the *x*-variable).

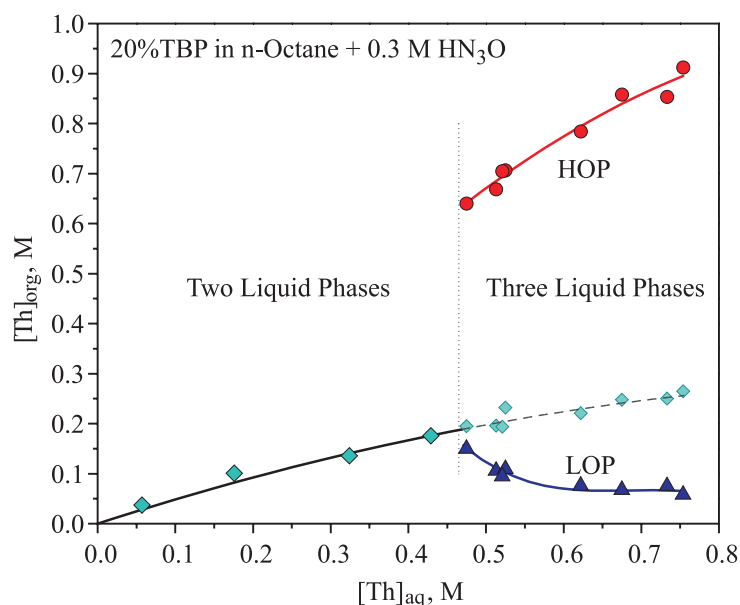


Fig. 1. An isotherm of thorium(IV) extraction in the system  $\text{Th}(\text{NO}_3)_4/\text{HNO}_3/20\%\text{TBP}$  in *n*-octane. The concentration of nitric acid in the organic phase was equal to  $0.30 \pm 0.02$  M maintained by a sufficient concentration of nitric acid in the aqueous phase. Thorium concentrations in the three liquid phase region (diamonds) were calculated as a weighted average for the entire organic phase.

In the system presented in Figure 1, for  $\text{Th}(\text{NO}_3)_4$  concentrations in the organic phase above 0.19 M, which corresponds to 0.47 M of the equilibrium thorium concentration in the aqueous phase, the single organic phase is no longer stable and splits into two organic phases. The 0.19 M  $\text{Th}(\text{NO}_3)_4$  concentration in the organic phase is called a limit of organic concentration, LOC, in this system. The thorium concentration in the heavy organic phase is much greater than in the light organic phase, and also the TBP concentration is much greater in the HOP. Particular attention should also be paid to one more characteristic plotted on this graph. When these two organic phases, LOP plus HOP, are treated as a one homogeneous organic phase, the calculated thorium concentrations in the organic phase are

a smooth continuation of the thorium extraction isotherm (dashed line in Figure 1). This is an indication, that after the organic phase is split there is no exchange of solute between the organic and aqueous phases.

In this new approach only the  $y$ -variable is changed. The present work demonstrates a new approach that does not use an aqueous phase for splitting the organic phase into two organic phases. This system can be treated as two liquids with limited miscibility, i.e. limited mutual solubility. One of the liquid is an extractant loaded with inorganic compound(s) (salt or acid), strongly polar and the second is a non-polar aliphatic diluent. The polar liquid can be prepared e.g. by dissolution thorium nitrate in (pure) TBP. To demonstrate the new approach, a simple system consisting with TBP and nitric acid was selected. Nitric acid was introduced to 100% TBP by performing three consecutive extractions of the concentrated nitric acid (~15 M). The composition of the polar liquid was close to  $\text{TBP}\cdot 1.6\text{HNO}_3$ . If a higher concentration of nitric acid in TBP is required, fuming nitric acid must be used. A small aliquot of 0.5 mL of the polar liquid was transferred to a graduated cylinder and the aliphatic diluent, *n*-dodecane, was added in small portions. The results of this experiment are presented in Figure 2.

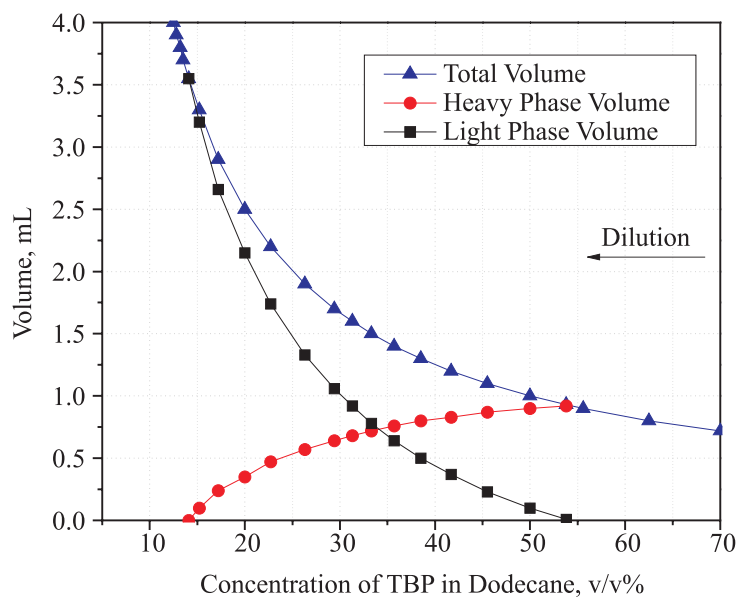


Fig. 2. Experimentally determined volumes of the heavy and light phases, and the total volume of the system consisting of  $\text{TBP}\cdot 1.6\text{HNO}_3$  and *n*-dodecane.

Only one organic phase was observed while the concentration of the polar phase in dodecane decreased from 100% to 54% v/v. After the polar phase concentration in dodecane dropped below 54% v/v a second organic phase appeared. This new phase showed up on top of the existing organic phase, therefore, it was called the light phase. Its volume was very small. Further addition of the diluent influenced the ratio of the light to heavy organic phase. The volume of the heavy organic phase continuously decreased and the volume of the light organic phase continuously increased with each addition of diluent. When the concentration of the polar phase reached 14% v/v both phases combined, forming a single organic phase. By these measurements the upper and lower limits of miscibility were determined.

Assuming that the concentration of the polar liquid in the heavy organic phase was constant and equal to 54% v/v (the upper LOC) and knowing the volumes of both the light and heavy phases, the polar liquid concentration in the light phase resulting from each dilution was calculated from the mass balance. In Table 1 the calculated concentrations are listed. The average calculated concentration of the polar liquid in the light phase was equal to  $14.1 \pm 0.4\%$  v/v and was equal to lower LOC.

Table 1. Concentrations of the polar liquid in the light organic phase (LOP) calculated using assumption that the concentration of the polar liquid in the heavy organic phase (HOP) is constant, equal to 54% v/v (upper LOC).

Average TBP cntr v/v %	Volume Total mL	Volume HOP mL	Volume LOP mL	TBP conc. in LOP v/v %
55.6	0.90	0	0	
53.8	0.93	0.92	0.01	14.0
50.0	1.00	0.90	0.10	13.1
45.5	1.10	0.87	0.23	14.0
41.7	1.20	0.83	0.37	13.6
38.5	1.30	0.80	0.50	14.0
35.7	1.40	0.76	0.64	14.3
33.3	1.50	0.72	0.78	14.4
31.3	1.60	0.68	0.92	14.6
29.4	1.70	0.64	1.06	14.5
26.3	1.90	0.57	1.33	14.3
22.7	2.20	0.47	1.74	14.5
20.0	2.50	0.35	2.15	13.9
17.2	2.90	0.24	2.66	13.9
15.2	3.30	0.10	3.20	14.1
14.1	3.55	0	0	
Average				14.1
St. Dev.				0.4

Concentrations of TBP in the light and heavy phase were different; however, from the data presented in Table 1 one can conclude that they were constant in each of the phases. The distribution of nitric acid between the light and heavy phase should be proportional to the TBP concentrations. If TBP concentrations in the HOP and LOP within the area of limited miscibility (Figure 3) were equal to 54% and 14% respectively, thereafter the stoichiometry of the polar liquid in each of the phases should be conserved (equal to the initial stoichiometry). This hypothesis requires further analytical work investigating the area of limited miscibility.

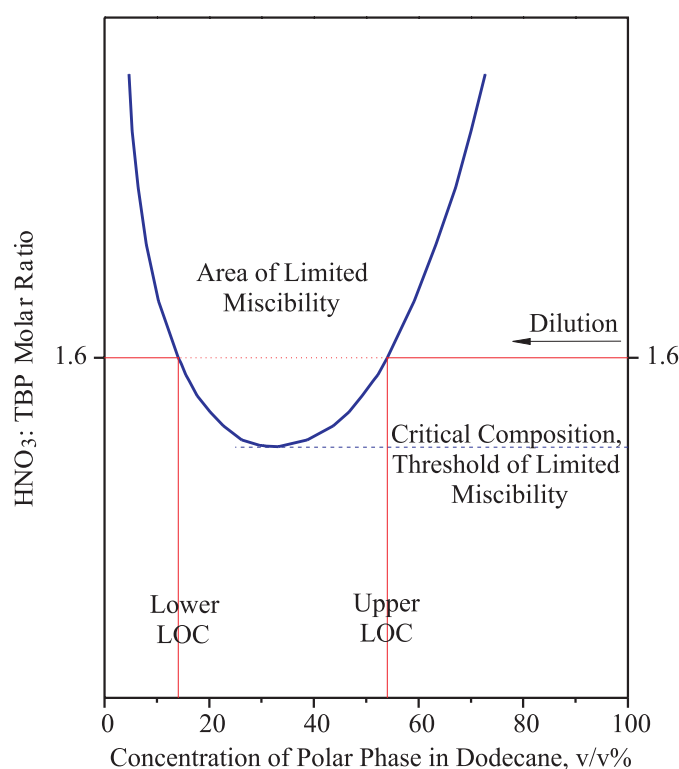


Fig. 3. Example of a diagram describing a limited miscibility of the polar liquid with a non-polar diluent. The Upper LOC and Lower LOC are measured during serial dilutions. The threshold of limited miscibility indicates critical composition of the polar liquid, below which only a single phase is observed over the entire range of dilutions.

This new approach gives other simple opportunities for the measurement of the parameters affecting formation of third phases. In the investigated system the prepared polar liquid had the composition:

TBP·1.6HNO<sub>3</sub>. A small addition of pure TBP to this polar liquid will result in a different stoichiometry and a new polar liquid is obtained. Instead of the TBP·1.6HNO<sub>3</sub>, other polar liquids with compositions: TBP·1.5HNO<sub>3</sub>, or TBP·1.4HNO<sub>3</sub> can be easily prepared. Using these new polar liquids and repeating the procedure described above, the upper and lower limit of miscibility for these new compositions of polar liquids can be determined. With decreasing polarity of the polar liquid (less nitric acid) and for *n*-dodecane used as the diluent, the difference between the upper and lower limits will be reduced, compared to TBP·1.6HNO<sub>3</sub> system. Finally, a single phase over the entire range of TBP concentrations in *n*-dodecane will be observed when HNO<sub>3</sub> to TBP molar ratios are below 1.18 [11]. The expected shape of the curve describing the TBP/HNO<sub>3</sub>/dodecane system is presented in Figure 3. The minimum on the curve corresponds to the critical composition, the threshold required for third phase formation. This value may be critical for the third phase prediction and might be applied for third phase modeling using a computer code in which the minimum energy for one and two phase systems can be calculated.

The behavior of these liquids is consistent with the Baxter's sticky sphere model [19,20]. Schematically these two phases are presented in Figure 4.

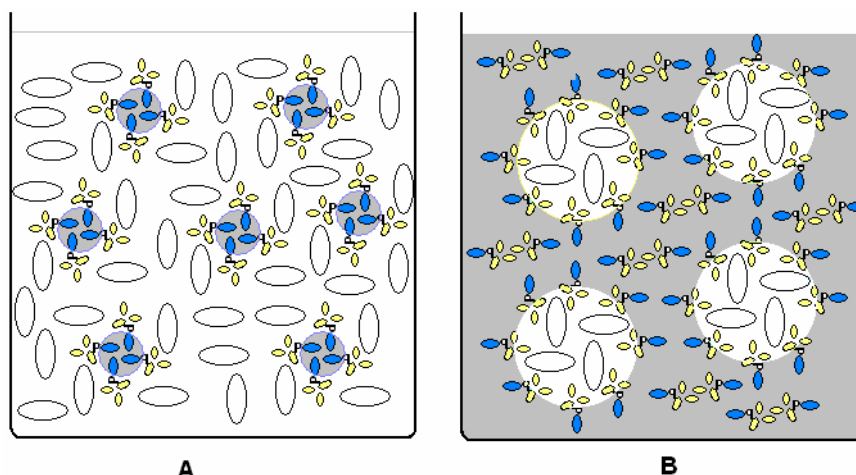


Fig. 4. Graphical representation of organic solutions consisting of the same components but having different concentrations. A) At low concentrations of polar liquid micelles with the polar cores are formed; B) At high concentrations of polar liquid reverse micelles with non-polar cores are formed. If the transition from state A to state B cannot be done smoothly, the system splits into two immiscible phases. The phase A conversion to the phase B can be imagined as flipping an umbrella during the wind.

In the heavy phase, the diluent and the polar liquid form reverse micelles, where the non-polar diluent is closed in the micelle core and surrounded by the polar liquid. When the capacity of the micelle core for the non-polar diluent is exceeded a light phase is ejected. The structure of the micelles in the light phase is reversed to the micelles in the heavy phase. The micelles with polar cores are surrounded by non-polar diluent. When the polarity of the polar liquid decreases and reaches the critical composition, the reverse micelles (with non-polar core) can smoothly be converted into regular micelles (with polar core) and the second phase is not formed.

The effect of other aliphatic diluents on third phase formation in TBP with  $\text{HNO}_3$  system can be easily measured using the same approach but instead of dodecane, aliphatic hydrocarbons are used as diluents. The analogous curve to Figure 3 will be shifted up to higher  $\text{HNO}_3$  : TBP molar ratios with decreasing numbers of carbons in the aliphatic hydrocarbons used.

Finally, the effect of an inorganic salt (e.g.  $\text{Th}(\text{NO}_3)_4$ ,  $\text{Pu}(\text{NO}_3)_4$  or  $\text{UO}_2(\text{NO}_3)_2$ , etc.) on third phase formation may be investigated using the same approach. This introduces an additional variable to the existing system, and the picture switches from two dimensional to three dimensional. The salt concentration is the  $z$ -variable, perpendicular to the plane describing behavior of this simple system. The three dimensional system could be the next stage in the third phase investigation, but first, a mathematical model for simple systems have to be successfully developed.

### CONCLUSIONS

A new approach for third phase investigation is described in this paper. This new approach eliminates the aqueous phase simplifying the system to give new insight in the nature of the third phase. The experimental results for the system containing TBP·1.6 $\text{HNO}_3$  and  $n$ -dodecane demonstrate utility of this easy method. From the real miscibility diagram, which example is presented in Figure 3, the behavior of the  $\text{HNO}_3$ /TBP/ $n$ -dodecane system at any  $\text{HNO}_3$  concentration and any concentration of TBP in  $n$ -dodecane can be predicted. The new approach is a step forward in understanding of the mechanism governing the formation of third phase. This new approach could quickly provide sufficient data to develop a comprehensive mathematical model. Species in such systems exhibit positive deviations from Raoult's Law and perhaps the liquid activities may be derived from the one parameter Margules model.



## REFERENCES

- [1] Healy T.V., McKay H.A.C., 1956. The Extraction of Nitrates by Tri-n-butyl Phosphate (TBP). Part 2 – The Nature of the TBP Phase. *Trans. Faraday Soc.* 52, 633-642.
- [2] Mills A.L., Logan W.R., 1967. Third Phase Formation Between Some Actinide Nitrates and 20% Tri-n-butyl Phosphate/Odourless Kerosene. [In:] *Solvent Extraction Chemistry*. D. Dyrssen, J.-O. Liliejin, J. Rydberg (Eds.), Gothenburg 1966, North Holland, Amsterdam, 322-326.
- [3] Solovkin A.S., Povitskii N.S., Lunichkina K.P., 1960. Formation of Third Phase in the System  $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-Tri-n-butyl Phosphate-Kerosene}$ . *Russ. J. Inorg. Chem.* 5(9), 1026-1028 (English Transl.).
- [4] Zilberman B.Ya., Fedorov Yu.S., Kopyrin A.A., Arkipov S.A., Blazheva I.V., Glekov R.G., 2001. Extraction of U(IV) and U(VI) with 30% Tributyl Phosphate under Conditions of Formation of the Second Organic Phase. *Radiochemistry* 43(2), 172-176 (Translation from *Radiokhimiya*).
- [5] Vasudeva Rao P.R., Kolarik Z.A., 1996. Review of Third Phase Formation in Extraction of Actinides by Neutral Organophosphorus Extractants. *Solvent Extr. Ion Exch.* 14(6), 955-993.
- [6] Kertes A.S., 1965. The Chemistry of the Formation and Elimination of a Third Phase in Organophosphorus and Amine Extraction Systems. [In:] *Solvent Extraction Chemistry of Metals*. Macmillan, London, 377-399.
- [7] Francois L., Belnet F., Noel D., Tondre C., 1999. An Attempt to Theoretically Predict Third-Phase Formation in the Dimethyldibutyltetradecylmalonamide (DMDBTDMA)/Dodecane/Water-Nitric Acid Extraction System. *Sep. Sci. Technol.* 34(5), 755-770.
- [8] Hu Z., Hu X., Cui W., Wang D., Fu X., 1999. Three Phase Extraction Study. II. TBP-Kerosene/ $\text{H}_2\text{SO}_4\text{-TiOSO}_4$  System and the Preparation of Ultrafine Powder of  $\text{TiO}_2$ . *Colloids Surf. A* 155(2-3), 383-393.
- [9] Yang C., Chen J., 1996. Preparation and Characterization of Ultrafine  $\text{ZrO}_2$  Powders from Solvent Extraction of Zr(IV) with Tri-n-butyl Phosphate in Kerosene from Nitric Acid Solutions. *J. Mater. Sci. Technol.* 12(6), 439-444.
- [10] Hu Z., Pan Y., Ma W., 1995. Purification of Organophosphorus Acid Extractants. *Solvent Extr. Ion Exch.* 13(5), 965-976.
- [11] Shaekers J.M., 1991. Extraction of Inorganic Acids. [In:] *Science and Technology of Tributyl Phosphate*; W.W. Schulz, J.D. Navratil, A.S. Kertes (Eds.), Vol. IV, CRC Press, Boca Raton, Florida, 71-204.
- [12] Boukis N., Kanellakopoulos B., 1983. Extractive Phase Distribution of Uranyl Nitrate with Tri-n-butyl Phosphate. II. Formation of a Third Phase in the Uranyl Nitrate – Tri-n-butyl Phosphate (TBP) Nitric Acid System. *Kernforschungszentrum, Rep. KFK-3352*; Karlsruhe: Federal Republic of Germany.
- [13] Kolarik Z., 1979. The Formation of a Third Phase in the Extraction of Pu(IV), U(IV), and Th(IV) Nitrates with Tributyl Phosphate an Alkane Diluents. *ISEC'77. CIM Spec. Vol. 21*, Can. Inst. Mining Metallurgy, Toronto, Canada, 178-189.
- [14] Ferraro J.R., Borkowski M., Chiarizia R., McAlister D.R., 2001. FT-IR Spectroscopy of Nitric Acid in TBP/Octane Solution. *Solvent Extr. Ion Exch.* 19(6), 981-992.
- [15] Borkowski M., Ferraro J.R., Chiarizia R., McAlister D.R., 2002. FT-IR Study of Third Phase Formation in the U(VI) or Th(IV)/ $\text{HNO}_3$ , TBP/Alkane Systems, *Solvent Extr. Ion Exch.* 20(3), 313-330.
- [16] Chiarizia R., Jensen M.P., Borkowski M., Ferraro J.R., Thiyagarajan P., Littrell K.C., 2003. Study of Third Phase Formation in TBP Solvent Extraction System. *Solvent Extr. Ion Exch.* 21(1), 1-27.

- [17] Borkowski M., Chiarizia R., Jensen M.P., Ferraro J.R., Thiyagarajan P., Littrel K.C., 2003. Third Phase Formation Revisited: The U(VI),HNO<sub>3</sub>/TBP-n-Octane System, *Separation Science & Technology* 38(12-23), 3333-3351.
- [18] Chiarizia R., Jensen M.P., Borkowski M., Ferraro J.R., Thiyagarajan P., Littrel K.C., 2003. SANS Study of Third Phase Formation in the U(VI)-HNO<sub>3</sub>-TBP-n-Dodecane System, *Separation Science & Technology* 38(12-23), 3313-3331.
- [19] Chiarizia R., Jensen M.P., Rickert P.G., Kolarik Z., Borkowski M., Thiyagarajan P., 2004. Extraction of Zirconium Nitrate by TBP in n-Octane: Influence of Cation Type on Third Phase Formation According to the "Sticky Spheres" Model. *Langmuir* 20, 10798-10808.
- [20] Chiarizia R., Jensen M.P., Borkowski M., Thiyagarajan P., Littrell K.C., 2004. Interpretation of third phase in the Th(IV)-HNO<sub>3</sub>/TBP-n-octane system with Baxter's "Sticky Spheres" Model. *Solvent Extr. Ion Exch.* 22(3), 325-351.
- [21] Jensen M.P., Chiarizia R., Ferraro J.R., Borkowski M., Nash K.L., Thiyagarajan P., Littrel K.C., 2002. New Insights in third Phase Formation in the U(VI)-HNO<sub>3</sub>/TBP-Alkane System, *Proceedings of ISEC 2002*, Cape Town, South Africa. K.C. Sole, P.M. Cole, J.S. Preston, D.J. Robinson (Eds.), South African Institute of Mining and Metallurgy, Marshalltown, RSA. 1137-1142.
- [22] Chiarizia R., Thiyagarajan P., Jensen M.P., Borkowski M., Littrel K.C., 2003. Study of Third Phase Formation in TBP Solvent Extraction System as a Result of Interaction Between Reverse Micelles. *Proceedings of Intern. Symposium on Hydrometallurgy*, Vancouver, Canada, 917-928.