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## Phosphoric acid recovery from concentrated aqueous feeds by a mixture of di-isopropyl ether (DiPE) and tri-*n*-butylphosphate (TBP): extraction data and modelling

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This paper reports experimental data about the extraction of phosphoric acid from concentrated aqueous feeds (3 to 14 M H<sub>3</sub>PO<sub>4</sub>) by the mixture of di-isopropyl ether (DiPE) and tri-*n*-butylphosphate (TBP) at 25 °C: distribution ratios of H<sub>3</sub>PO<sub>4</sub> and water, and change of phase volume ratio during extraction. Then, a simple model based on the extraction isotherms of H<sub>3</sub>PO<sub>4</sub> and water as well as on the mass balance of these two compounds is developed in the case of the mixture of 90% wt DiPE and 10% wt TBP that corresponds to the solvent used at the industrial scale for the production of purified phosphoric acid.

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### Introduction

Phosphoric acid is a weak oxyacid with many industrial applications depending on its degree of purification. Phosphate ore contains many impurities such as calcium, iron, aluminium, fluorine, uranium, *etc.* Therefore, it is mandatory to implement efficient purification processes to produce purified phosphoric acid for different applications. Merchant grade Phosphoric Acid (MPA) is employed in surface treatments and in the production of fertilizers. Food grade Phosphoric Acid (FPA) is used in the production of salts for animal feeding or in the acidulation of food and drinks for human consumption. Pharmaceutical grade Phosphoric Acid (PPA) is produced for the pharmaceutical industry. From the current production of phosphate ores, 137.6 Mt per year,<sup>1</sup> less than 4% is for food and pharmaceutical industries but these two sectors need high-grade phosphoric acid.

Phosphoric acid can be produced from phosphate ores by two main processes: (i) pyrometallurgical or thermal processes, which use phosphorus as an intermediate material and issue a pharmaceutical grade phosphoric acid, and (ii) hydrometallurgical or wet processes involving leaching, solvent extraction and precipitation stages. In the thermal process, phosphorus is first produced by reduction of the phosphate rock, followed by re-oxidation and hydration to give phosphoric acid. Despite the production of a very high-grade phosphoric acid, the thermal route has been progressively abandoned due to its prohibitive

energetic cost (only 5% of the total phosphoric acid was produced by thermal processes in 2007).<sup>2</sup> In the wet process, phosphate, ores are leached with a mineral acid, usually sulfuric acid and the resulting leachate is further purified to produce higher grade phosphoric acid. Currently, several hydrometallurgical techniques, including precipitation,<sup>3</sup> adsorption,<sup>4,5</sup> ion exchange,<sup>6</sup> reverse osmosis,<sup>7</sup> nanofiltration<sup>8</sup> have been considered to achieve such a purification, and the best practical results are obtained when combining chemical and solvent extraction methods.

There are two main strategies for purifying phosphoric acid: (i) the elimination of the impurities or (ii) the selective extraction of H<sub>3</sub>PO<sub>4</sub>. Most of the oldest methods belong to the first category and are based on the precipitation of insoluble salts, even if the recovery of specific elements such as uranium attracts increasing attention.<sup>9–13</sup> Few examples are listed below:

- De-fluorination by precipitation of (Na,K)<sub>2</sub>SiF<sub>6</sub> or MgSiF<sub>6</sub>·6H<sub>2</sub>O.<sup>14</sup>
- Sulfate precipitation by adding calcium or barium salts at high temperature.<sup>15</sup>
- Heavy metal precipitation, for instance as sulfides (*e.g.*, CdS).<sup>16</sup>

Nowadays, most purification methods belong to the second category, *i.e.* the selective extraction of H<sub>3</sub>PO<sub>4</sub> against impurities. Various solvents based on functional groups including ethers,<sup>17–23</sup> alcohols,<sup>24–29</sup> ketones<sup>30–38</sup> or tri-alkylphosphates,<sup>38–43,43–49</sup> amines,<sup>11,50</sup> sulfoxides<sup>51,52</sup> used either individually or in synergetic mixtures, have been patented. These systems are listed in Table 1.

All of these solvents can extract more or less efficiently phosphoric acid as a result of the formation of hydrogen bonds between the extractant and phosphoric acid molecules. Water is co-extracted as well because hydrogen bonding can take place

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Table 1 Main patented processes industrially deployed for the purification of phosphoric acid

Process	Patent	Extractant	Feed solution	
			% P <sub>2</sub> O <sub>5</sub>	M
Prayon	US3970741 (1974) <sup>53</sup>	DIPE + TBP	61	14.2
Rhône-Poulenc	US4769226 (1987) <sup>54</sup>	TBP	<40	7.6
	EP0030487 (1985) <sup>55</sup>			
	US3304157 (1967) <sup>56</sup>			
IMI	US3304157 (1967) <sup>56</sup>	Ethers + alcohols	>35	6.4
	US3311450 (1967) <sup>57</sup>			
	US3573005 (1971) <sup>58</sup>			
Budenheim Toyo-Soda	US3920797 (1975) <sup>59</sup>	Iso-propanol	20–55	3.2–12
	US4154805 (1977) <sup>60</sup>	Butanol or iso-butanol	No restriction	
	US3529932 (1970) <sup>61</sup>			
Albright & Wilson	US3947499 (1976) <sup>62</sup>	MIBK	<62	14.2
	US3914382 (1975) <sup>63</sup>			
	US3912803 (1975) <sup>64</sup>			

between the molecules of water and those of extractant/diluent, but also because water and H<sub>3</sub>PO<sub>4</sub> can interact *via* hydrogen bonding.

Among these systems, the Prayon Process, based on the mixture of 90 wt% di-isopropylether (DiPE) and 10 wt% tri-*n*-butylphosphate (TBP) is the most used at the industrial scale, with feed solutions typically containing up to 14.2 M H<sub>3</sub>PO<sub>4</sub> (*i.e.*, 61.1% P<sub>2</sub>O<sub>5</sub>). In spite of a series of papers about the extraction of H<sub>3</sub>PO<sub>4</sub> from aqueous feeds by the mixture of DiPE (or other ethers) and TBP,<sup>65,66</sup> the physicochemistry of such systems is still not well understood, as far as the speciation of H<sub>3</sub>PO<sub>4</sub> in initial and equilibrated aqueous phase, the speciation of H<sub>3</sub>PO<sub>4</sub> in organic phase after extraction, the structure of the organic phases and its dependency on supramolecular phenomena (*e.g.*, 3<sup>rd</sup> phase formation), *etc.*, are concerned.

Regarding modelling of phosphoric acid extraction by organic solvents, only few studies are available in the literature and they are often limited to H<sub>3</sub>PO<sub>4</sub> concentrations lower than 8 mol L<sup>-1</sup>.<sup>88–92</sup> For instance, Ziat *et al.*<sup>91</sup> modelled the distribution of phosphoric acid between TBP and aqueous solution containing 0–6 mol kg<sup>-1</sup> phosphoric acid by means of a thermodynamic model accounting for activity coefficients of phosphoric acid in aqueous and organic phases by using the Pitzer's equation and the Sergievskii–Danus's relationship, respectively, and by considering the presence of the following species: TBP, TBP·H<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub>·TBP and (TBP)<sub>2</sub>·H<sub>3</sub>PO<sub>4</sub>·H<sub>2</sub>O. Although these representations describe accurately the thermodynamics of these systems (speciation, activity coefficients), and in certain cases the extraction phenomena, they are limited from low to moderate ionic strengths media and require the adjustment of many parameters, which have almost no physical-sense.

Likewise, Hamdi and Hannachi<sup>92</sup> published a simulation of extraction, washing and stripping stages of a WPA purification process using tri-*n*-butyl phosphate (TBP), methyl isobutyl ketone (MIBK) and their mixture (MIBK + TBP) as extraction solvent. This model was based on the use of extraction isotherms for calculating the number of theoretical stages and the content of acid and impurities in the two phases for each step of the purification process. However, this paper does not

give detailed information about the model used and does not predict phase volume changes throughout the extraction whereas volume variations can be particularly high as shown in the present paper.

The objectives of the present paper are to (i) briefly review this physicochemistry, (ii) provide additional extraction data and (iii) propose a model of mass transfer for the mixture of industrial interest that contains 90 wt% di-isopropylether (DiPE) and 10 wt% tri-*n*-butylphosphate (TBP). The present paper is focused on the modelling of phosphoric acid extraction and not on the modelling of phosphoric acid stripping from DiPE–TBP as the latter is not at all an issue. Indeed, full phosphoric acid stripping can be easily achieved simply by contacting the loaded extraction solvent DIPE + TBP with water at temperature close to 40 °C in order to break hydrogen bonds.

This model is based on the use of the distribution isotherms of H<sub>3</sub>PO<sub>4</sub> and water previously determined by a limited series of experiments. This model has been used for predicting the yield of extraction of H<sub>3</sub>PO<sub>4</sub> and the associated variations of phase volumes (shrinking and swelling of the aqueous and organic phases, respectively) under more general conditions, including the variation of the initial phase volume ratio of the aqueous and organic phases.

## Experimental

### Materials

TBP (purity > 97%) and DIPE (purity > 98.5%) were both supplied by Sigma-Aldrich and used without further purification. The extraction was performed using a series of phosphoric acid solutions with concentrations ranging from 3 up to 14 M and prepared by dilution from concentrated phosphoric acid (VWR, AnalaR NORMAPUR 85% wt H<sub>3</sub>PO<sub>4</sub>) with water purified by a Milli-Q Gradient system from Millipore Corporation (resistivity > 18.2 MΩ cm). The concentrations of the initial solutions were verified by means of acid–base titration with 1 M NaOH (concentration verified using potassium hydrogen phthalate, ACS primary standard). Wet Phosphoric Acid (WPA) used in this work was supplied by Prayon.



## Solvent extraction procedure

Liquid–liquid extraction of phosphoric acid was carried out by contacting an organic phase containing 10% wt TBP in DIPE with a series of phosphoric acid solutions for which initial concentrations varied from 3 to 14 M and initial phase volume ratio was equal to  $O/A = 6$  (organic phase volume over aqueous phase volume), unless otherwise stated. Aqueous and organic phases were shaken during 1 hour at  $(25.0 \pm 0.2)^\circ\text{C}$  at a shaking frequency of  $120\text{ min}^{-1}$  with a mechanical shaking apparatus (Gherardt Laboshake) thermostated with a Gherardt Thermoshake ( $\text{H}_3\text{PO}_4$  extraction equilibria were reached within less than 10 minutes of contact). The mixture was settled for 30 minutes. After phase disengagement, the aqueous phase was separated and the organic phase was filtered by using a Whatman 1 PS filter before being analysed. Volume changes of each phase were observed during phosphoric acid extraction. They were particularly high for the aqueous phase.

Phosphoric acid concentrations in aqueous and organic solutions were determined by acid–base titration using a 780 Metrohm pH Meter equipped with a glass electrode with 1.00 M and 5.85 M NaOH (NaOH concentration was checked before titration by using potassium hydrogen phthalate, ACS primary standard). For the organic phase, biphasic titrations were performed by dispersing a weighted amount of the sample in water.

Water concentrations in the organic phases were determined by the Karl–Fischer method using a V20 Mettler-Toledo Karl–Fischer titrator. Hydranal-Methanol Rapid (Fluka Analytical) and Hydranal-Composite 5 (Fluka Analytical) were used as reagents. The calibration was performed by using Hydranal-Water Standard 10.0 (Fluka Analytical, water concentration in the standard of  $10.05 \pm 0.03\text{ g kg}^{-1}$ ).

The volumes of the aqueous and organic phases after equilibration were deduced from their weights and densities (measured with a pycnometer).

Experiments were performed in duplicate and errors on aqueous and organic concentrations of  $\text{H}_3\text{PO}_4$  and water are about 2% and 5%, respectively.

## Computing

Computer simulations were carried out on a PC with the free mathematical software Scilab<sup>67</sup>. The set of mass balance equations for the calculation of the extraction equilibria was solved by the Powell method implemented in Scilab<sup>67</sup>.

## Results and discussion

### Physicochemical behaviours: state of the art

**$\text{H}_3\text{PO}_4$  in the aqueous feed solutions.** The speciation of phosphoric acid in aqueous solutions has been investigated by various authors. Dartiguelongue *et al.* have recently concluded after Elmore *et al.* and Messnaoui and Bounahmidi that phosphoric acid exists as  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{PO}_4^-$  and  $\text{H}_5\text{P}_2\text{O}_8^-$  (dimeric species) in 0–6 M solutions, where the concentration of  $\text{H}_5\text{P}_2\text{O}_8^-$  increases as the total concentration of acid is

increased.<sup>68–70</sup> These species are dissolved in the aqueous phase *via* hydrogen bonding within the network of water molecules. Above about 6 M  $\text{H}_3\text{PO}_4$ , the speciation studies are much scarcer. On the other hand, there is a consensus that the water activity ( $a_w$ ) sharply decreases from 6 M  $\text{H}_3\text{PO}_4$  (e.g.,  $a_w = 0.7367$  at  $9.1863\text{ mol kg}^{-1}$ , i.e., 6.3 M, at  $25^\circ\text{C}$ ) to 15 M  $\text{H}_3\text{PO}_4$  (e.g.,  $a_w = 0.0957$  at  $57.265\text{ mol kg}^{-1}$ , i.e., 14.6 M, at  $25^\circ\text{C}$ ).<sup>70–73</sup> It is of interest that at 6.3 M  $\text{H}_3\text{PO}_4$ , the molar ratio  $\text{H}_2\text{O}/\text{H}_3\text{PO}_4$  is equal to about 6, which means that  $\text{H}_3\text{PO}_4$  is dissolved in the network of water *via* hydrogen bonding, whereas at 14.6 M  $\text{H}_3\text{PO}_4$ , the molar ratio  $\text{H}_2\text{O}/\text{H}_3\text{PO}_4$  has decreased to about 1. In fact, at 6.3 M  $\text{H}_3\text{PO}_4$ , the structure of the continuous hydrogen-bond based network encountered in pure water has certainly been deeply modified as most hydrogen bonds between water molecules should have been broken and new bonds between  $\text{H}_3\text{PO}_4$  and water molecules should have been extensively formed. Close to 14.6 M  $\text{H}_3\text{PO}_4$ , we reach the transition from a  $\text{H}_3\text{PO}_4$ -in-water network to a water-in- $\text{H}_3\text{PO}_4$  network. Such a decrease of the molar ratio  $\text{H}_2\text{O}/\text{H}_3\text{PO}_4$  and the associated modifications of the structure of the aqueous solution implies that phosphoric acid is less and less retained in the latter by hydrogen bonding with water.

**Extraction of  $\text{H}_3\text{PO}_4$  by DiPE (or other ethers).** The extraction of  $\text{H}_3\text{PO}_4$  by ethers (DiPE, *n*-propyl-iso-propyl ether, di-*n*-propyl ether, *etc.*) used alone has been studied by several authors.<sup>18–21,23,74,75</sup> The extraction begins at about 10 M  $\text{H}_3\text{PO}_4$  (i.e. 66% wt) with a sharp increase above (Fig. 1).

Ethers belong to the family of compounds containing donor atoms (here oxygen) but no active hydrogen atoms. They are polar (e.g.,  $\mu = 1.18\text{ D}$  for diethyl ether compared to 1.85 D for water) and form a network by  $\alpha$ -multimerization (Fig. 2).

Phosphoric acid is extracted in ethers by formation of a complex containing one molecule of water as expressed by the following chemical formula for DiPE:  $\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2$  where  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{O}$  and ether molecules are linked together by hydrogen bonds.<sup>74</sup>

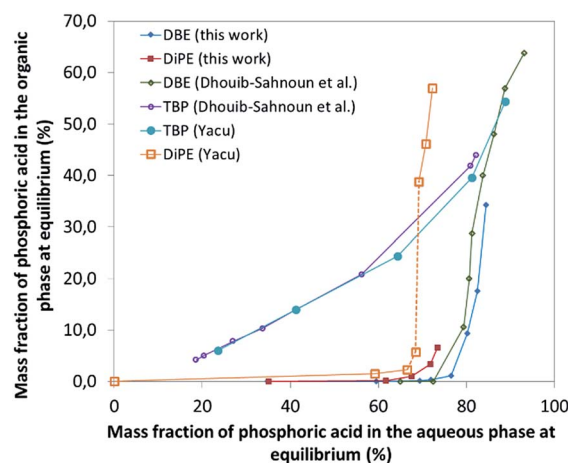


Fig. 1 Extraction isotherms of  $\text{H}_3\text{PO}_4$  from aqueous feed by various solvents (this work, Dhouib-Sahnoun,<sup>46</sup> Yacu<sup>74</sup>). In the case of DiPE, the dotted part of the extraction curve corresponds to a domain where 3<sup>rd</sup> phase formation is observed.



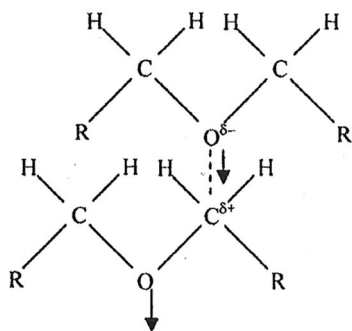


Fig. 2 Head-tail arrangement in diethyl ether leading to  $\alpha$ -multimerization.<sup>75</sup> Adapted with permission from (S. K. Pradhan, S. K. Dash, L. Moharana and B. B. Swain, *Indian J. Pure Appl. Sci.*, 2012, 50, 161–166). Copyright (2012) Indian Journal of Pure & Applied Physics.

In the formation of the preceding complex, there is a competition between ether and water molecules to form hydrogen bonds with  $\text{H}_3\text{PO}_4$ . It is of interest that the extraction of  $\text{H}_3\text{PO}_4$  becomes significant only when its concentration in aqueous phase is very high (>8 M) which corresponds to the region where the hydrogen-bond based network of water is dramatically modified by insertion of the  $\text{H}_3\text{PO}_4$  molecules, to reach at the end a water-in- $\text{H}_3\text{PO}_4$  network. Unfortunately, such  $\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O} \cdot \text{ether}$  complexes formed for instance with DiPE and diethyl ether are poorly soluble both in aqueous solutions and in excess ether, which leads to the formation of third phases (*i.e.*, to the splitting of the organic phase into a light organic phase mainly containing ether and a heavy organic phase containing the complex  $\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O} \cdot \text{ether}$ ). Nevertheless, with ethers possessing longer alkyl chains, such as dibutyl ether (DBE), no third phase formation is observed. To delay the formation of such third phases occurring with ethers possessing short chains, including DiPE, phase modifiers can be added, as for instance TBP.

**Extraction of  $\text{H}_3\text{PO}_4$  by TBP.** The extraction of  $\text{H}_3\text{PO}_4$  by TBP has been investigated by various authors.<sup>42,45,46,76–78</sup> As can be seen in Fig. 1, the extraction of  $\text{H}_3\text{PO}_4$  by TBP is much more gradual than with DiPE or DBE, as extraction is effective even from diluted phosphoric acid solution. TBP is a solvating extractant used at the industrial scale for the reprocessing of spent nuclear fuel.<sup>79</sup> Its molecule is more basic than that of ethers and thus can compete much more efficiently than the latter with the molecules of water, to form a complex *via* hydrogen bonding. In rather diluted media (*i.e.*, 0–6 mol kg<sup>-1</sup> [about 0–4.6 M]), Ziat *et al.* have concluded that the extraction of  $\text{H}_3\text{PO}_4$  and water in pure TBP takes place by formation of the following species:  $\text{TBP} \cdot \text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_4 \cdot \text{TBP}$  and  $(\text{TBP})_2 \cdot \text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ .<sup>77</sup> Bhouib-Sahnoun *et al.* have studied the extraction of  $\text{H}_3\text{PO}_4$  and water by TBP in a larger range of acidity (*i.e.*, 0–15.5 M) and with TBP either used pure or diluted in toluene.<sup>46</sup> These authors concluded that the composition of the extracted complex ranges between  $(\text{TBP})_2 \cdot \text{H}_3\text{PO}_4$  and  $\text{TBP} \cdot \text{H}_3\text{PO}_4$  (water molecules are omitted) depending upon the amount of TBP present in the organic phase. A molar ratio  $[\text{H}_3\text{PO}_4]_{\text{org}}/[\text{TBP}]_{\text{org}}$  of 4 was even reached in highly concentrated aqueous media

(>15 M  $\text{H}_3\text{PO}_4$ ) and pure TBP, which was attributed to the formation of aggregates. It should be recalled here that TBP is known to form aggregates in apolar diluents.<sup>49,80–82</sup> Furthermore, Dhouib-Sahnoun *et al.* have re-investigated the extraction of water and observed, in contradiction with Higgins *et al.*<sup>78</sup> that the molar ratio  $[\text{H}_2\text{O}]_{\text{org}}/[\text{TBP}]_{\text{org}}$  monotonically decreases as the ratio  $[\text{H}_3\text{PO}_4]_{\text{org}}/[\text{TBP}]_{\text{org}}$  increases from 0 to 1 in pure TBP and concluded that such a behaviour tends to indicate that  $\text{H}_3\text{PO}_4$  is extracted as an anhydrous species, which competes with water in the P → O sites of the TBP phase. On the other hand, they observed that the molar ratio  $[\text{H}_2\text{O}]_{\text{org}}/[\text{TBP}]_{\text{org}}$  increases as the ratio  $[\text{H}_3\text{PO}_4]_{\text{org}}/[\text{TBP}]_{\text{org}}$  increases from 1 to 4 and concluded that water is then probably extracted as a hydrated complex of phosphoric acid associated with aggregate formation in the TBP phase (cross linkages) at the highest organic acidities. Concerning the molar ratio  $[\text{H}_3\text{PO}_4]_{\text{org}}/[\text{TBP}]_{\text{org}}$  of 4 found in highly concentrated aqueous media (>15 M  $\text{H}_3\text{PO}_4$ ), it is of interest that Kim *et al.* have reported theoretical studies on the structure and the hydrogen-bond strength of trimethyl phosphate-( $\text{HNO}_3$ )<sub>n</sub> complexes,  $n = 1–3$ , to model the TBP-( $\text{HNO}_3$ )<sub>n</sub> complexes.<sup>83</sup>

**Extraction of  $\text{H}_3\text{PO}_4$  by the mixtures of DiPE and TBP.** As TBP is rather viscous, it is often diluted in diluents such as alkanes (*e.g.*, kerosene<sup>76</sup>). However, TBP is also sometimes used as a phase modifier to prevent/delay the formation of third phases. The Prayon process is based on the use of a mixture of 90 wt% di-isopropylether (DiPE) and 10 wt% tri-*n*-butylphosphate (TBP), both to enhance the extraction of  $\text{H}_3\text{PO}_4$  compared to DiPE and to prevent the formation of third phases. On the other hand, Shlewit and Alibrahim have used the mixture of 1/9 ratio of DiPE/TBP in 20% kerosene, claimed as synergistic.<sup>65,66</sup> The behaviour of the extraction of  $\text{H}_3\text{PO}_4$  with the mixtures of di-isopropylether (DiPE) and tri-*n*-butylphosphate (TBP) are further investigated below.

### Experimental study of the extraction of $\text{H}_3\text{PO}_4$ and $\text{H}_2\text{O}$ by the mixtures of DiPE and TBP

In this part of the work, most experiments have been performed with AnalaR NORMAPUR phosphoric acid.

The extraction isotherms of phosphoric acid and water are displayed in Fig. 3 (top and below). These figures show that the extraction of phosphoric acid increases all the more rapidly with aqueous  $\text{H}_3\text{PO}_4$  concentration that the concentration of TBP in the mixture DiPE + TBP is high, in coherence with the respective affinity of DiPE and TBP for  $\text{H}_3\text{PO}_4$  as reported in Fig. 1. It of interest that the molar ratio  $[\text{H}_3\text{PO}_4]_{\text{org}}/[\text{TBP}]_{\text{org}}$  related to  $\text{H}_3\text{PO}_4$  extracted by TBP (after subtraction of  $\text{H}_3\text{PO}_4$  extracted by DiPE) reaches values of 2 at point A and even 4 at point B and 6 at point C. For points B and C, such values are rather high and would normally be expected at higher  $\text{H}_3\text{PO}_4$  concentration as reported by Dhouib-Sahnoun *et al.*<sup>46</sup> (Fig. 1). On the other hand, at point A, the value of 2 found for the molar ratio  $[\text{H}_3\text{PO}_4]_{\text{org}}/[\text{TBP}]_{\text{org}}$  at point A is in agreement with the findings of these authors.<sup>46</sup> It also appears that the amount of water extracted into the organic phase exhibits a pseudo-plateau region (with a soft decrease) between 0 and about 7 M  $\text{H}_3\text{PO}_4$  (see especially 0.28 M TBP isotherm) and then a sharp increase. This pseudo-



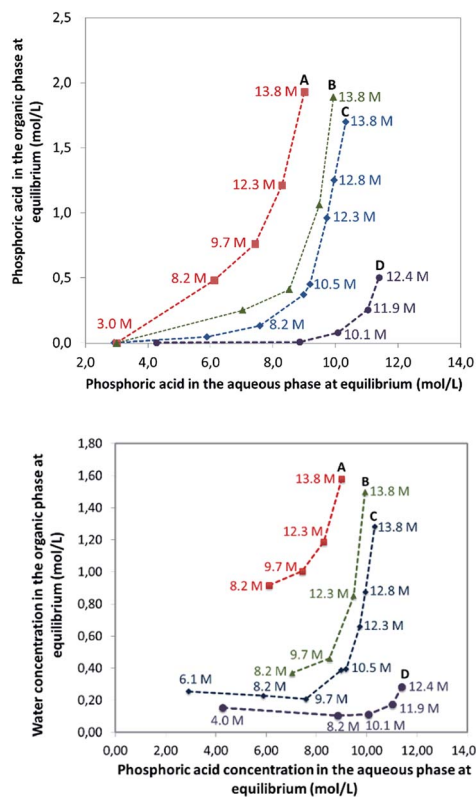


Fig. 3 Extraction isotherms of phosphoric acid (top) and water (below) at 25 °C. Aqueous phase: analytical phosphoric acid for which initial concentration ranges from 3 to 13.8 M. Organic phase: mixture of TBP (0.28 M indicated by blue diamonds, 0.45 M indicated by green triangles, 1.00 M indicated by red squares). The initial volumes for the organic phase were about 200 mL and the initial phase volume ratio  $O/A = 6$  (phase volume ratios at equilibrium are quite different from initial phase volume ratios due to phosphoric acid and water extraction). Numbers in the graph correspond to the initial concentrations of phosphoric acid in the aqueous phase.

plateau region where the extraction of  $H_3PO_4$  is low corresponds mainly to the solubilisation of water by DiPE (0.22 M water at 25 °C)<sup>84</sup> and TBP (3.59 M water at 25 °C).<sup>85</sup> The amount of water solubilized in organic phase in this range of aqueous  $H_3PO_4$  concentration is all the higher that the concentration of TBP in the mixture DiPE + TBP is high. Above about 7 M  $H_3PO_4$ , water extraction follows that of phosphoric acid, but with molar ratio  $[H_2O]_{org}/[H_3PO_4]_{org}$  lower than one (e.g., close to 0.7).

The extraction of  $H_3PO_4$  and water from the aqueous phase to the organic phase implies an important increase of their phase volume ratios  $O/A$  compared to the initial values (Fig. 4). As expected, the concentration of  $H_3PO_4$  in the raffinate decreases during extraction, but due the shrinking of the aqueous phase, the final concentration in the raffinate may remain rather high (e.g., from initially 13.8 M to 8.5 M in point A of Fig. 3), thus the water activity of the system increases during the extraction, which may have consequences on the salting-out effect and the extraction of metal impurities.<sup>86,87</sup>

As said above, WPA contains many impurities. However, the presence of such impurities has little effect on the extraction of  $H_3PO_4$  as shown in Fig. 5.

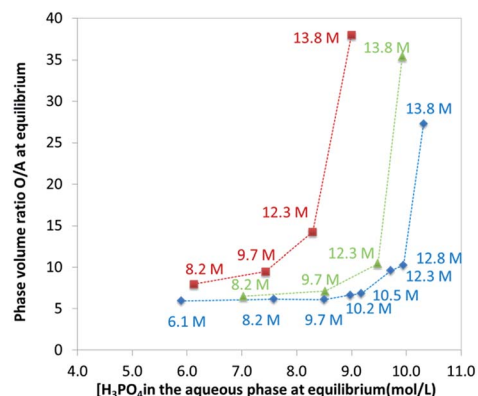


Fig. 4 Phase volume ratio at equilibrium plotted against the phosphoric acid concentration at equilibrium in the aqueous phase. Aqueous phase: analytical phosphoric acid which initial concentration ranges between 3 and 13.8 M. Organic phase: mixture of TBP (0.45 M indicated by green triangles, 1 M indicated by red squares, 0.28 M indicated by blue diamonds) in DiPE. See Fig. 3 for experimental conditions. Numbers in the graph correspond to initial concentration of phosphoric acid in the aqueous phase.

### Modelling of the extraction of $H_3PO_4$ and $H_2O$ by the mixture of DiPE (90 wt%) and TBP (10 wt%)

**Description of the model.** This model uses extraction isotherms of phosphoric acid and water by 0.28 mol L<sup>-1</sup> TBP in DiPE (Fig. 3) as well as mass balance equations. On the other hand, the variations of phase volume are not used as input data, but calculated by the model.

As a first approximation, it is assumed in this model that the volume conservation is satisfied as expressed below:

$$V_T = V_{0,aq} + V_{0,org} = V_{eq,aq} + V_{eq,org} \quad (1)$$

where  $V_T$  denotes the initial total volume that is considered as constant during extraction,  $V_{0,aq}$  and  $V_{0,org}$  represent initial volumes of the aqueous and organic phases, respectively, and

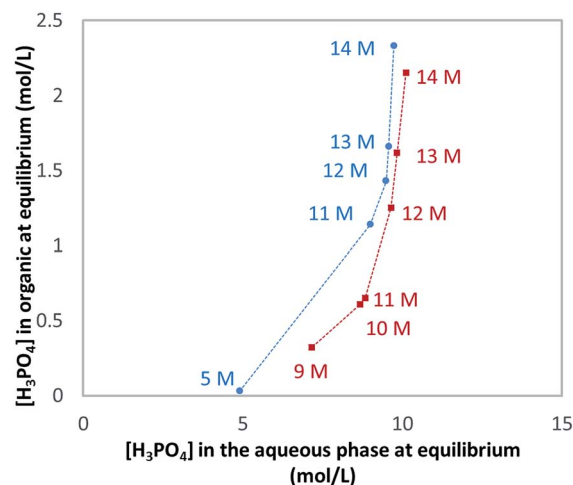


Fig. 5 Extraction isotherms of synthetic phosphoric (blue dots) and WPA (red squares) at 25 °C: Wet Phosphoric Acid (WPA) provided by Prayon. Organic phase: 0.28 M TBP in DiPE. Initial volumes for the organic phase = 400 mL; initial phase volume ratio = 6.



$V_{\text{eq,aq}}$  and  $V_{\text{eq,org}}$  denote the volume at equilibrium of the aqueous and organic phases, respectively.

Mass balance of  $\text{H}_3\text{PO}_4$  can be written and completed by a volume balance of each phase which takes into account water extraction:

$$V_{0,\text{aq}}x_0 = V_{\text{eq,aq}}x + V_{\text{eq,org}}y \quad (2)$$

$$V_{\text{eq,org}} = V_{0,\text{org}} + V_{\text{eq,org}}y \times v_{\text{mp}}^* + V_{\text{eq,org}}z \times v_{\text{me}}^* \quad (3)$$

$$V_{\text{eq,aq}} = V_{0,\text{aq}} - V_{\text{eq,org}}y \times v_{\text{mp}}^* - V_{\text{eq,org}}z \times v_{\text{me}}^* \quad (4)$$

where,  $x_0$  and  $x$  stands for  $\text{H}_3\text{PO}_4$  concentrations initially and at equilibrium, respectively. In these equations,  $y$  and  $z$  denote  $\text{H}_3\text{PO}_4$  and water concentrations at equilibrium in the organic phase, respectively,  $v_{\text{mp}}^*$  represents the molar volume of phosphoric acid ( $v_{\text{mp}}^* = 0.053 \text{ L mol}^{-1}$ ) and  $v_{\text{me}}^*$  corresponds to the molar volume of water ( $v_{\text{me}}^* = 0.018 \text{ L mol}^{-1}$ ).

In this paper, it is assumed that the solubility of DIPE and TBP in the aqueous phase is sufficiently low to be neglected. Indeed, the solubility of di-isopropyl ether and TBP in water are equal  $2 \text{ g L}^{-1}$  at  $20^\circ\text{C}$  and  $0.4 \text{ g L}^{-1}$  at  $25^\circ\text{C}$ , respectively.

Phosphoric acid and water extraction are described in the present paper by two extraction isotherms  $y = f_{\text{H}_3\text{PO}_4}(x)$  and  $z = f_{\text{H}_2\text{O}}(x)$ , respectively, where  $x$  denotes phosphoric acid concentration in aqueous phase at the equilibrium.

By using eqn (1)–(3) and the extraction isotherms  $y = f_{\text{H}_3\text{PO}_4}(x)$  and  $z = f_{\text{H}_2\text{O}}(x)$ , the following expression can be written:

$$\begin{aligned} x \times \left[ V_{0,\text{aq}} - \left( \frac{V_{0,\text{org}}}{1 - f_{\text{H}_3\text{PO}_4}(x) \times v_{\text{mp}}^* - f_{\text{H}_2\text{O}}(x) \times v_{\text{me}}^*} f_{\text{H}_3\text{PO}_4}(x) \right. \right. \\ \left. \left. \times v_{\text{mp}}^* - \frac{V_{0,\text{org}}}{1 - f_{\text{H}_3\text{PO}_4}(x) \times v_{\text{mp}}^* - f_{\text{H}_2\text{O}}(x) \times v_{\text{me}}^*} f_{\text{H}_2\text{O}}(x) \times v_{\text{me}}^* \right) \right] \\ + f_{\text{H}_3\text{PO}_4}(x) \times \left[ \frac{V_{0,\text{org}}}{1 - f_{\text{H}_3\text{PO}_4}(x) \times v_{\text{mp}}^* - f_{\text{H}_2\text{O}}(x) \times v_{\text{me}}^*} \right] \\ - V_{0,\text{aq}}x_0 = 0 \end{aligned} \quad (5)$$

Phosphoric acid and water concentrations in the aqueous and organic phases at the equilibrium can be deduced from eqn (5) for any initial conditions. Afterwards, it is thus possible to determine the volumes of the organic and aqueous phases at the equilibrium by means of eqn (6) and (7):

$$V_{\text{eq,org}} = \frac{V_{0,\text{org}}}{1 - f_{\text{H}_3\text{PO}_4}(x) \times v_{\text{mp}}^* - f_{\text{H}_2\text{O}}(x) \times v_{\text{me}}^*} \quad (6)$$

$$\begin{aligned} V_{\text{eq,aq}} = V_{0,\text{aq}} - \left( \frac{V_{0,\text{org}}}{1 - f_{\text{H}_3\text{PO}_4}(x) \times v_{\text{mp}}^* - f_{\text{H}_2\text{O}}(x) \times v_{\text{me}}^*} f_{\text{H}_3\text{PO}_4}(x) \right. \\ \left. \times v_{\text{mp}}^* - \frac{V_{0,\text{org}}}{1 - f_{\text{H}_3\text{PO}_4}(x) \times v_{\text{mp}}^* - f_{\text{H}_2\text{O}}(x) \times v_{\text{me}}^*} f_{\text{H}_2\text{O}}(x) \times v_{\text{me}}^* \right) \end{aligned} \quad (7)$$

**Input data: extraction isotherms of phosphoric acid and water.** Extraction isotherms  $y = f_{\text{H}_3\text{PO}_4}(x)$  and  $z = f_{\text{H}_2\text{O}}(x)$  can be simulated by using an empirical law as illustrated in Fig. 6.

$$y = f_{\text{H}_3\text{PO}_4}(x) = 2.5 \times 10^{-4} e^{0.855x} \quad (\text{with } x \text{ and } y \text{ in M}) \quad (8)$$

$$z = f_{\text{H}_2\text{O}}(x) = 1.5 \times 10^{-9} e^{1.98x} + 0.25 \quad (\text{with } x \text{ and } z \text{ in M}) \quad (9)$$

**Application of the model.** Fig. 7 shows a good agreement between experimental values of phosphoric acid concentration at equilibrium in the aqueous phase and those calculated with the present model. Likewise, a good agreement is obtained between experimental data and the model for describing the variation of the phase volume ratios at equilibrium vs. initial phosphoric acid concentration.

Fig. 8 shows that this model can also be used to calculate the extraction yield of phosphoric acid as a function of the phase volume ratio at equilibrium for different initial phase volume ratios. It should be noted that the plot is derived from the model, and that the variations of volumes measured experimentally were not introduced in the model. There is a good agreement between the model and the experiments.

In order to evaluate the model and assess its ability to represent experimental data, calculated values  $Z_{\text{calc}}$ , *i.e.*

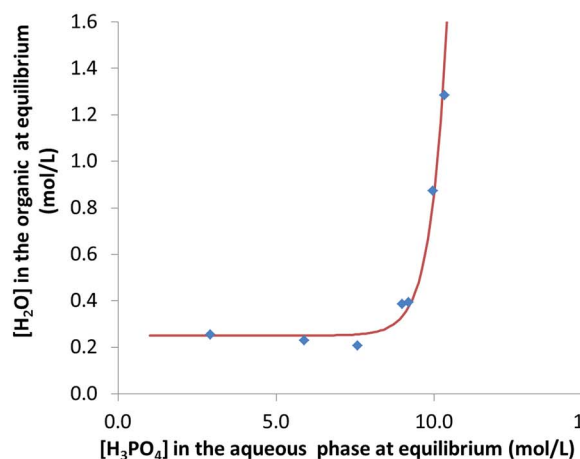
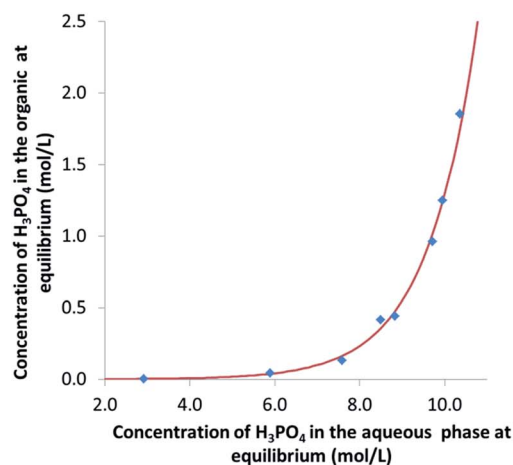


Fig. 6 Experimental data and simulated curves derived from eqn (8) and (9) for the extraction of phosphoric acid (top) and water (below). Aqueous phase: 3–14 M phosphoric acid; organic phase: 0.28 M TBP in DIPE.



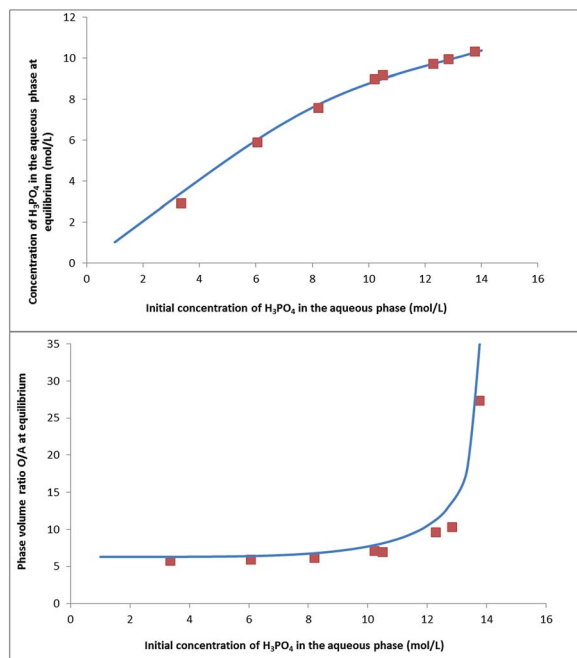


Fig. 7 Experimental data (red squares) and simulated curves (blue line) of phosphoric acid concentration in the raffinate (top) and phase volume ratio (below) at equilibrium, as a function of the initial concentration of phosphoric acid in the aqueous phase. Input parameters for the model:  $V_{0, \text{aq}} = 0.1$  L,  $V_{0, \text{org}} = 0.6$  L.

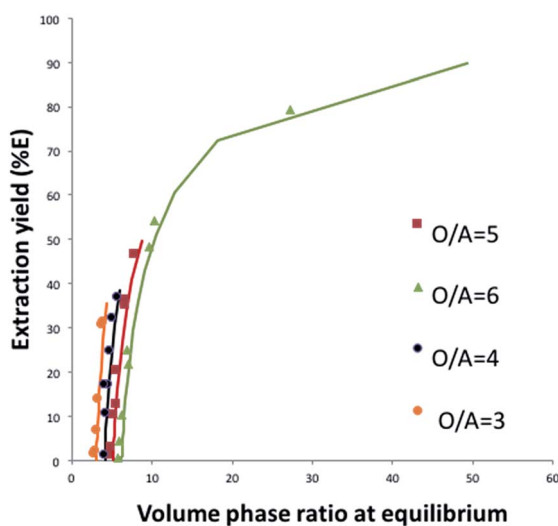


Fig. 8 Experimental and predicted phosphoric acid extraction efficiency as a function of the phase volume ratio at the equilibrium, for different initial phase volume ratios (O/A) and at constant TBP concentration (0.28 M). (Line = values calculated by the present model; squares, triangles and circles = experimental data.) Input parameters for the model:  $V_{0, \text{aq}} = 0.1$  L,  $V_{0, \text{org}} = 0.6$  L.

calculated phosphoric acid concentration in organic phase, calculated extraction yield or calculated phase volume ratio, have been plotted as a function of the experimental values  $Z_{\text{exp}}$ , *i.e.* experimental phosphoric acid concentration in organic phase, experimental extraction yield or experimental phase

Table 2 Quality indicators for the model deduced from Fig. 8

	$[\text{H}_3\text{PO}_4]_{\text{aq}}^a$	$[\text{H}_3\text{PO}_4]_{\text{org}}^a$	$\text{O/A}^a$	$[\text{H}_2\text{O}]_{\text{org}}^a$
<b>O/A = 7</b>				
$R^2$	0.9345	0.8259	1.0868	1.0132
$u$	1.0589	0.9358	0.9424	0.9753
<b>O/A = 6</b>				
$R^2$	1.0042	0.974	—	—
$u$	0.9936	0.9056	—	—
<b>O/A = 5</b>				
$R^2$	0.9888	0.9718	0.926	0.966
$u$	0.9674	0.9255	0.8847	1.1012
<b>O/A = 4</b>				
$R^2$	0.9915	0.9688	0.9280	0.9677
$u$	1.0407	0.9204	0.9439	1.1344
<b>O/A = 3</b>				
$R^2$	0.9941	0.995	0.7644	0.983
$u$	1.0489	0.7455	0.9171	1.0398

<sup>a</sup> At equilibrium.

volume ratio. The equation of  $Z_{\text{calc}} = F(Z_{\text{exp}})$  can be expressed as follows:

$$Z_{\text{calc}} = uZ_{\text{exp}} \quad (10)$$

The slope  $u$  and the standard deviation  $R^2$  for eqn (9) are good indicators for the quality of the model. These values should be equal to unity if the model was in perfect agreement with the experimental data. Table 2 gathers  $u$  and  $R^2$  values for different experiments. These values confirm the accuracy of the model to predict experimental data.

## Conclusions

The extraction of  $\text{H}_3\text{PO}_4$  and water by the mixtures of DiPE and TBP has been revisited and the obtained results indicate that the speciation in organic phase is more complex than the  $\text{H}_3\text{-PO}_4 \cdot \text{H}_2\text{O} \cdot \text{ether}$  species reported previously. A simple model based on the extraction isotherms of  $\text{H}_3\text{PO}_4$  and water as well as on the mass balance of these two compounds is developed in the case of the mixture of 90% wt DIPE and 10% wt TBP which corresponds to the solvent used at the industrial scale for the production of purified phosphoric acid. The model can be used for optimization of the operational conditions.

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## Notes and references

- 1 S. J. Van Kauwenbergh, M. Stewart and R. Mikkelsen, *Better Crops*, 2013, **97**, 18–20.



- 2 N. S. Awwad, Y. A. El-Nadi and M. M. Hamed, *Chem. Eng. Process.*, 2013, **74**, 69–74.
- 3 R. Kijkowska, D. Pawlowska-Kozinska, Z. Kowalski, M. Jodko and Z. Wzorek, *Sep. Purif. Technol.*, 2002, **28**, 197–205.
- 4 L. Monser, M. Ben Amor and M. Ksibi, *Chem. Eng. Process.*, 1999, **38**, 267–271.
- 5 A. A. Daifullah, N. Awwad and S. El-Reefy, *Chem. Eng. Process.*, 2004, **43**, 193–201.
- 6 D. W. Agers, J. E. House, J. L. Drobnick and C. J. Lewis, *Hydrometallurgy*, 1963, 515–529.
- 7 J. Yu and D. Liu, *Chem. Eng. Res. Des.*, 2010, **88**, 712–717.
- 8 H. Diallo, M. Rabiller-Baudry, K. Khaless and B. Chaufer, *J. Membr. Sci.*, 2013, **427**, 37–47.
- 9 D. Beltrami, G. Cote, H. Mokhtari, B. Courtaud and A. Chagnes, *Hydrometallurgy*, 2012, **129**, 118–125.
- 10 D. Beltrami, A. Chagnes, M. Haddad, A. Varnek, H. Mokhtari, B. Courtaud and G. Cote, *Hydrometallurgy*, 2013, **140**, 28–33.
- 11 D. Beltrami, G. Cote, H. Mokhtari, B. Courtaud, B. A. Moyer and A. Chagnes, *Chem. Rev.*, 2014, **114**, 12002–12023.
- 12 D. Beltrami, A. Chagnes, M. Haddad, H. Laureano, H. Mokhtari, B. Courtaud, S. Juge and G. Cote, *Hydrometallurgy*, 2014, **144**, 207–214.
- 13 D. Beltrami, A. Chagnes, M. Haddad, H. Laureano, H. Mokhtari, B. Courtaud, S. Juge and G. Cote, *Sep. Sci. Technol.*, 2013, **48**, 480–486.
- 14 A. M. B. Freitas and M. Giulietti, *Nutr. Cycling Agroecosyst.*, 1997, **48**, 235–240.
- 15 M. Kikuchi and Y. Hiraga, US4041134A, 1977, p. 5.
- 16 E. Ennaassia, K. El Kacemi, A. Kossir and G. Cote, *Hydrometallurgy*, 2002, **64**, 101–109.
- 17 C. H. Harrison and P. Roquero, *J. Chem. Eng. Data*, 2004, **49**, 218–220.
- 18 C. H. Harrison and P. Roquero, *J. Chem. Eng. Data*, 2004, **49**, 218–220.
- 19 F. Ruiz, A. Marcilla, A. Ancheta and C. Rico, *Solvent Extr. Ion Exch.*, 1986, **4**, 789–802.
- 20 F. Ruiz, A. Marcilla, A. Ancheta and C. Rico, *Solvent Extr. Ion Exch.*, 1986, **4**, 771–787.
- 21 A. Marcilla, F. Ruiz, J. Campos and M. Asensio, *Solvent Extr. Ion Exch.*, 1989, **7**, 201–210.
- 22 A. Marcilla, F. Ruiz, J. Campus and M. Asensio, *Solvent Extr. Ion Exch.*, 1989, **7**, 211–221.
- 23 F. Ruiz, A. Marcilla and A. M. Ancheta, *Solvent Extr. Ion Exch.*, 1987, **5**, 1141–1150.
- 24 D. Maljković, D. Maljković and A. Paulin, *Solvent Extr. Ion Exch.*, 1992, **10**, 477–489.
- 25 S. Khorfan, O. Shino and A. Wahoud, *Chem. Eng.*, 2003, **45**, 139–148.
- 26 H. G. Gilani, A. G. Gilani, S. Shekarsaraee and H. Uslu, *Fluid Phase Equilib.*, 2012, **316**, 109–116.
- 27 A. Gómez-Siurana, F. Ruiz-Beviá, J. Fernández-Sempere and E. Torregrosa-Fuerte, *Ind. Eng. Chem. Res.*, 2001, **40**, 892–897.
- 28 F. Ruiz, A. Marcilla, A. M. Ancheta and J. A. Caro, *Solvent Extr. Ion Exch.*, 1985, **3**, 331–343.
- 29 H. Ghannadzadeh and K. Ghannadzadeh, in *Computational Methods in Applied Science and Engineering*, ed. A. K. Haghi, Nova Science Publishers, Inc, Hauppauge, 2010, pp. 95–105.
- 30 M. Feki and H. F. Ayedi, *Can. J. Chem. Eng.*, 2000, **78**, 540–546.
- 31 H. G. Gilani, A. G. Gilani and S. Shekarsaraee, *Fluid Phase Equilib.*, 2013, **337**, 32–38.
- 32 A. Marcilla, F. Ruiz and D. Martinezpons, *Solvent Extr. Ion Exch.*, 1993, **11**, 469–485.
- 33 J. Saji and M. L. P. Reddy, *Hydrometallurgy*, 2001, **61**, 81–87.
- 34 A. Marcilla, F. Rulz and D. Martinez-Pons, *Solvent Extr. Ion Exch.*, 1993, **11**, 455–467.
- 35 M. Feki, M. Fourati, M. M. Chaabouni and H. F. Ayedi, *Can. J. Chem. Eng.*, 1994, **72**, 939–944.
- 36 M. Feki and H. F. Ayedi, *Sep. Sci. Technol.*, 1998, **33**, 2609–2622.
- 37 A. Hannachi, D. Habaili, C. Chtara and A. Ratel, *Sep. Purif. Technol.*, 2007, **55**, 212–216.
- 38 R. Hamdi and A. Hannachi, *J. Chem. Eng. Process Technol*, 2012, **3**, 134.
- 39 J. J. Čomor, M. M. Kopećni and D. M. Petkovic, *Solvent Extraction and Ion Exchange*, 2007, **15**, 991–1006.
- 40 A. Marcilla and F. Ruiz-Bevia, *J. Chem. Eng. Data*, 2014, **59**, 2693–2694.
- 41 J. Mu, R. Motokawa, C. D. Williams, K. Akutsu, S. Nishitsuji and A. J. Masters, *J. Phys. Chem. B*, 2016, **120**, 5183–5519.
- 42 M. Alibrahim, *Period. Polytech., Chem. Eng.*, 2007, **51**, 39–42.
- 43 Y. Jin, J. Li, J. Luo, D. Zheng and L. Liu, *J. Chem. Eng. Data*, 2010, **55**, 3196–3199.
- 44 C. Liu, J. Cao, W. Shen, Y. Ren, W. Mu and X. Ding, *Fluid Phase Equilib.*, 2016, **408**, 190–195.
- 45 K. Ziat, B. Messnaoui, T. Bounahmidi, M. de la Guardia and S. Garrigues, *Fluid Phase Equilib.*, 2004, **224**, 39–46.
- 46 R. Dhouib-Sahnoun, M. Feki and H. F. Ayedi, *J. Chem. Eng. Data*, 2002, **47**, 861–866.
- 47 E. Hesford and H. A. C. McKay, *J. Inorg. Nucl. Chem.*, 1960, **13**, 156–164.
- 48 M. Abdulkake and O. Shino, *Period. Polytech., Chem. Eng.*, 2007, **51**, 3.
- 49 X. Fu, J. Shi, Y. Zhu and Z. Hu, *Solvent Extr. Ion Exch.*, 2002, **20**, 241–250.
- 50 S. A. Rodrigues, *Curso de Pos-Graduacao em Engenharia Metalurgica e Minas*, Universidade Federal de Minas Gerais, 2011.
- 51 Z. R. Toregozhina, M. R. Tanasheva and B. A. Beremzhanov, *Zh. Neorg. Khim.*, 1981, **26**, 1419–1422.
- 52 S. Yuanfu and J. Yuming, EP0176613 A1, 1986.
- 53 E. W. Pavonet, US3970741A, 1976, p. 5.
- 54 L. Winand and D. Perron, US4769226 A, 1988.
- 55 L. Winand, EP0030487 (A1), 1981.
- 56 A. M. Baniel and B. Ruth, US3304157 A, 1967.
- 57 A. Alexander, A. M. Baniel, C. Mount and B. Ruth, US3311450 A, 1967.
- 58 A. M. Baniel and R. Blumberg, US3573005A, 1971.
- 59 S. Fujii, T. Nakajima and I. Toshimitsu, US3920797 A, 1975, p. 7.
- 60 Y. Hiraga and M. Kikuchi, US4154805 A, 1979, p. 6.



- 61 R. Imoto, M. Kikuchi and T. Sakomura, US3529932 A, 1970.
- 62 R. H. Edwards, T. A. Williams and K. Hall, US3947499 A, 1976.
- 63 T. A. Williams, US3914382 A, 1975.
- 64 F. M. Cussons and T. A. Williams, US3912803 A, 1975.
- 65 H. Shlewit and M. Alibrahim, *Period. Polytech., Chem. Eng.*, 2008, **52**, 7.
- 66 H. Shlewit, M. Alibrahim and A. Aoudi, *Solvent Extr. Res. Dev., Jpn.*, 2004, **11**, 11–20.
- 67 INRIA-ENPC, *Scilab*, Copyright© 1989–2005, www.scilab.org.
- 68 A. Dartiguelongue, E. Provost, A. Chagnes, G. Cote and W. Fürst, *Solvent Extr. Ion Exch.*, 2016, **34**, 241–259.
- 69 K. L. Elmore, J. D. Hatfield, R. L. Dunn and A. D. Jones, *J. Phys. Chem.*, 1965, **69**, 3520–3525.
- 70 B. Messnaoui and T. Bounahmidi, *Fluid Phase Equilib.*, 2005, **237**, 77–85.
- 71 K. L. Elmore, C. M. Mason and J. H. Christensen, *J. Am. Chem. Soc.*, 1946, **68**, 2528–2532.
- 72 C. Jiang, *Chem. Eng. Sci.*, 1996, **51**, 689–693.
- 73 H. Yang, Z. Zhao, D. Zeng and R. Yin, *J. Solution Chem.*, 2016, **45**, 1580–1587.
- 74 W. A. Yacu, PhD thesis, University of Aston in Birmingham, August 1997, [http://www.eprints.aston.ac.uk/10090/1/Yacu1977\\_845408.pdf](http://www.eprints.aston.ac.uk/10090/1/Yacu1977_845408.pdf), accessed on 17 December 2016.
- 75 S. K. Pradhan, S. K. Dash, L. Moharana and B. B. Swain, *Indian J. Pure Appl. Phys.*, 2012, **50**, 161–166.
- 76 H. Shlewit and S. A. Khorfan, *Solvent Extr. Res. Dev., Jpn.*, 2002, **9**, 59–68.
- 77 K. Ziat, B. Mesnaoui, T. Bounahmidi, R. Boussen, M. de la Guardia and S. Garrigues, *Fluid Phase Equilib.*, 2002, **201**, 259–267.
- 78 C. E. Higgins and W. H. Baldwin, *J. Inorg. Nucl. Chem.*, 1962, **24**, 415–427.
- 79 E. R. Irish and W. H. Reas, The Purex process – a solvent extraction reprocessing method for irradiated uranium, *Hanford Atomic Products Operation*, Richland, Washington, 1957.
- 80 M. R. Antonio, R. Chiarizia and F. Jaffrenou, *Sep. Sci. Technol.*, 2010, **45**, 1689–1698.
- 81 R. Chiarizia, A. Briand, M. P. Jensen and P. Thiyagarajan, *Solvent Extr. Ion Exch.*, 2008, **26**, 333–359.
- 82 R. Motokawa, S. Suzuki, H. Ogawa, M. R. Antonio and T. Yaita, *J. Phys. Chem. B*, 2012, **116**, 1319–1327.
- 83 Y. Kim, H. Kim and K. Park, *Bull. Korean Chem. Soc.*, 2002, **23**, 1811–1815.
- 84 A. Mącznyński, D. G. Shaw, M. Góral and B. Wiśniewska-Gocłowska, *J. Phys. Chem. Ref. Data*, 2008, **37**, 1147–1168.
- 85 C. J. Hardy, D. Fairhurst, H. A. C. McKay and A. M. Willson, *Trans. Faraday Soc.*, 1964, **60**, 1626–1636.
- 86 G. Cote, A. Jakubiak, D. Bauer, J. Szymanowski, B. Mokili and C. Poitrenaud, *Solvent Extr. Ion Exch.*, 1994, **12**, 99–120.
- 87 G. Cote and A. Jakubiak, *Hydrometallurgy*, 1996, **43**, 277–286.
- 88 W. Fürst and H. Renon, *AIChE J.*, 1993, **39**, 335–343.
- 89 A. Dartiguelongue, E. Provost, A. Chagnes, G. Cote and W. Fürst, *Solvent Extr. Ion Exch.*, 2016, **34**(3), 241–259.
- 90 A. Dartiguelongue, A. Chagnes, E. Provost, G. Cote and W. Fürst, *Hydrometallurgy*, 2016, **165**, 57–63.
- 91 K. Ziat, B. Mesnaoui, T. Bounahmidi, R. Boussen, M. de la Guardia and S. Garrigues, *Fluid Phase Equilib.*, 2002, 259–267.
- 92 R. Hamdi and A. Hannachi, *J. Chem. Eng. Process Technol.*, 2012, **3**, 2, DOI: 10.4172/2157-7048.1000134.

