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Effects of structural changes of new organophosphorus cationic exchangers on a solvent extraction of cobalt, nickel and manganese from acidic chloride media†

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The effects of structural changes of organophosphorus cationic exchangers on metal-distribution curves (extraction efficiency *vs.* pH) have been investigated for the recovery of cobalt(II), nickel(II) and manganese(II) from acidic chloride solutions. By using alkyl groups with different branching and hydrophobicity and by including oxygen atoms in the hydrophobic chains of the cationic exchangers, it has been shown that the change of the chemical structure in the hydrophobic chains plays an important role in the extraction behaviours and causes more specifically a shift of the extraction curves to higher or lower pH depending on pK_a values of extracting agents (evaluated by using QSPR calculations), distribution constants of metal–ligand complexes between organic and aqueous phases and the formation constant of the metal–ligand complexes. Based on the present results, interest in the new cationic exchangers synthesized in the present work for cobalt(II), nickel(II) and manganese(II) separation is also discussed.

Introduction

Cobalt, nickel and manganese are the main components of the positive electrodes used in lithium-ion batteries (LiBs). Demand will likely strongly increase in the next few decades due to the emergence of electric vehicles since LiBs are considered to be the best choice for high energy density applications such as electric vehicles. In order to meet the world demand for cobalt, manganese and nickel, it is mandatory to exploit new primary deposits such as laterites, sulphide ores and sea nodules or to develop processes to recover these metals from secondary wastes such as spent LiBs.[1,2] However, these raw materials contain manganese, nickel and cobalt at various concentrations and their valorisation relies on the development of processes capable to perform efficient separation of these metals in spite of their very close extraction properties.[3–5] For this goal, liquid–liquid extraction appears as the best and the most appropriate technology. Many papers report the use of cationic exchangers such as Cyanex 272, D2EHPA, Cyanex 301 or Ionquest 801 alone or in mixture with other cationic exchangers, anionic exchangers or solvating agents.[6,7] Their extraction efficiency is quite dependent on the nature of the metal and their speciation in aqueous phase. Metal speciation depends on the nature of the inorganic acid used for leaching the ore. For instance, hydrochloric acid is preferred instead of sulphuric acid when ores are difficult to leach because chloride ions have stronger tendency to form metal complexes than sulphate ions.[8]

The most frequently used extracting agent for cobalt–nickel separation is Cyanex 272 (bis-(2,4,4-trimethylpentyl)phosphinic acid). However, this extractant exhibits a low separation factor between cobalt(II) and manganese(II) both from acidic sulphate and chloride media. Conversely, D2EHPA (bis-(2-ethyl-hexyl-phosphoric acid) is a suitable extractant for Co(II)–Mn(II) separation from acidic chloride media.[9] The $pH_{1/2}$ (pH for which the extraction efficiency is equal to 50%) for Mn(II), Co(II) and Ni(II) extraction from acidic chloride media are equal to 3.95, 4.30 and 6.65 when Cyanex 272 is used as extractant diluted in kerosene and 2.20, 3.30 and 3.83 when D2EHPA is employed instead of Cyanex 272, respectively (*vide infra*). Therefore, a large amount of alkaline solution such as sodium hydroxide must be added in the leach solution to adjust the pH so that a selective extraction could be achieved, especially when Cyanex 272 is used to separate Co(II) and Ni(II). In order to decrease the

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operational expenditure, the design of new extracting agents capable to recover and separate cobalt, nickel and manganese at low pH and in few stages is highly required.

Metal extraction by cationic exchangers usually occurs according to the following equation:[10]

$$M_{aq}^{2+} + 2\{HL\}_{org} = \{ML_2\}_{org} + 2H_{aq}^{+} \quad (1)$$

where M^{2+} is a metal such as Co^{2+}, Mn^{2+} or Ni^{2+} for instance, and "org" and "aq" denote the organic and aqueous phases, respectively.

The extraction constant (K_{ex}) of the previous equilibrium is defined as:

$$K_{ex} = [\{ML_2\}_{org}][H_{aq}^{+}]^2/([M_{aq}^{2+}][\{HL\}_{org}]^2) \quad (2)$$

The following chemical equilibria can be written to describe the system:

$$2\{HL\}_{org} = \{(HL)^2\}_{org}\ K_{dim} = [\{(HL)^2\}_{org}]/[\{HL\}_{org}]^2 \quad (3)$$

$$\{HL\}_{aq} = H_{aq}^{+} + L_{aq}^{-}\ K_a = [H_{aq}^{+}][L_{aq}^{-}]/[\{HL\}_{aq}] \quad (4)$$

$$M_{aq}^{2+} + 2L_{aq}^{-} = \{ML_2\}_{aq}\ \beta = [\{ML_2\}_{aq}]/([M_{aq}^{2+}][L_{aq}^{-}]^2) \quad (5)$$

$$\{ML_2\}_{aq} = \{ML_2\}_{org}\ K_{D,ML_2} = [\{ML_2\}_{org}]/[\{ML_2\}_{aq}] \quad (6)$$

The distribution coefficient $D = [\{ML_2\}_{org}]/[M_{aq}^{2+}]$ can be expressed by using eqn (2)–(6) as follows:

$$\log(D) = \log K_{D,ML_2} + \log \beta - 2pK_a + 2\log[\{HL\}_{org}] + 2pH \quad (7)$$

with $pK_a = -\log K_a$.

Thus, eqn (7) shows the extraction efficiency at constant pH of the aqueous phase and constant concentration of extractant in the organic phase is improved provided that: (i) the metal–ligand complex is very stable in the organic phase (high value of β), (ii) the metal–ligand complex is highly soluble in the organic phase (high value of K_{D,ML_2}) and (iii) the pK_a of the organophosphorus acid is as low as possible. The chemical structure of the extractants is particularly important as it influences its pK_a value, its affinity toward metals (steric hindrance, complexing properties) and its partition between organic and aqueous phases (hydrophobicity).

Therefore, the pK_a value is one of the main factors influencing the distribution coefficient (D) as illustrated in eqn (7). For new extracting agents, the experimental determination of pK_a is frequently cumbersome and complicated because of their low solubility in water. On the other hand, in order to estimate pK_a values (as well as distribution coefficients or dimerization constants), various regression models based on the linear free energy relationship (LFER) can be applied.[11–17] For example, these models were applied to predict or estimate a distribution constant of non-ionizable crown ethers and their benzo-derivatives in the organic/water system,[18] to describe selectivity towards alkali metal cations in the bulk liquid membrane[19] as well as to correlate the distribution, dimerization, and dissociation constants of dialkylorganophosphorous acidic extractants with the properties of solutes and solvents.[20,21] However, some values of the descriptors used in the model construction should be determined experimentally[22,23] or predicted from other regression models.[24–27] Moreover, for new substances (*e.g.* extractants), the descriptor values prediction can be associated with the extrapolation outside the range of the model space (applicability domain) and can result in an error in estimating these values.

Alternatively, for the pK_a values estimation, the quantitative structure–property relationships (QSPR) models based on molecular descriptors as the independent variables have been used.[28,29] In the 2D-QSPR models over 1200 molecular descriptors, derived from a two-dimensional graph representation of a molecule, can be calculated[30] and applied in the model formulation, whereas in the LFER models, a small set of descriptors (*e.g.* 5 or 6 Abraham solvation parameters) were used. However, in the QSPR modelling, the application of appropriate variable selection methods results in a significant reduction in the number of descriptors. Additionally, it enables also the prediction of a given physicochemical property inside the applicability domain.

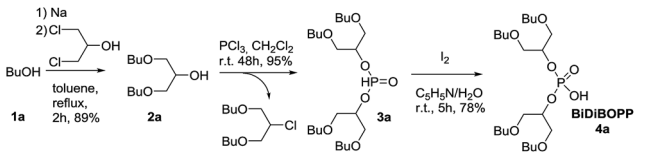
In the present paper, 2D-QSPR models based on multiple linear regression (MLR) and partial least square (PLS) methods[31] has been applied to predict pK_a values of new and commercial organophosphorus cationic exchangers in order to discuss the influence of their chemical structure on the extraction efficiency of Co(II), Ni(II) and Mn(II) *vs.* pH. In particular, the influence of branching, hydrophobicity and the presence of oxygen atoms in the hydrophobic chains has been investigated.

Experimental section

Synthesis of organophosphorus acids

Phosphorus trichloride (Fisher Scientific, purity 99%), pyridine (Fisher Scientific, purity 99%), 1-octanol (Fisher Scientific, purity 99%), 2-methyl-1-propanol (Fisher Scientific, purity 99%), 1-butanol (Fisher Scientific, purity 99.5%), lithium aluminium hydride (Fisher Scientific, purity 95%, powder), iodine (Fisher Scientific, purity 99%), sodium (Sigma Aldrich purity ≥ 99.8%), ethylene glycol butyl ether (Sigma Aldrich, purity ≥ 99%), 6-undecanone (TCI, purity > 98%), 2-ethyl-1-hexanol (TCI, purity > 99.5%) and 1,3-dichloro-2-propanol (TCI, purity > 98%) were used as delivered.

The synthesis of BiDiBOPP was performed according to the procedure previously published by Beltrami *et al.*[32] (Scheme 1).



Scheme 1 Synthesis route to BiDiBOPP as a sake of illustration of the general synthesis route of organophosphorus compounds synthesized in the present paper.

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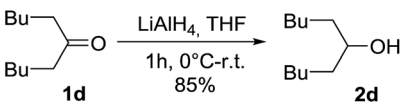
The 1,3-dibutoxy-2-propanol (**2a**) was synthesized by reaction of *n*-butanol and 1,3-dichloro-2-propanol in the presence of sodium metal. The reaction of **2a** with phosphorus trichloride (PCl_3) at room temperature led to bis(1,3-dibutoxypropan-2-yl)phosphite (**3a**) in a 78% yield. After purification, **3a** was oxidized by I_2 in pyridine–water mixture to form bis(1,3-dibutoxypropan-2-yl)phosphoric acid (BiDiBOPP, **4a**) (Scheme 1).

The cationic exchangers were synthesized by using the same procedure as for BiDiBOPP except for the synthesis of bis(undecan-6-yl)phosphoric acid (**4d**) (Table 1). Indeed, the corresponding alcohol **2d** used for the synthesis of **4d** was synthesized by reduction of undecan-6-on with lithium aluminium hydride $LiAlH_4$ at 0 °C in anhydrous THF according to the following reaction:



The reaction yield and the product purity determined by ^1H, ^{13}C, ^{31}P NMR spectroscopy are gathered in Table 1. The synthesized molecules were used in liquid–liquid extraction without any further purification.

Liquid–liquid extraction procedure

Aqueous phases. Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Sigma Aldrich, purity ≥ 98%), nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, Sigma Aldrich, purity ≥ 98%), manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, Sigma Aldrich, purity ≥ 98%), lithium chloride (Sigma-Aldrich, purity ReagentPlus) were used to prepare feed solutions for liquid–liquid extraction experiments.

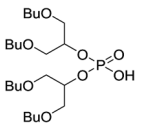
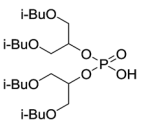
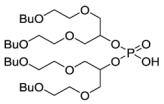
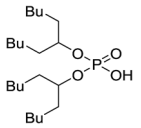
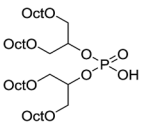
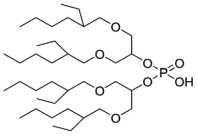
Feed solutions of Ni(II), Co(II) and Mn(II) at 1.17 g L^{-1} (0.02 mol L^{-1}), 1.18 g L^{-1} (0.02 mol L^{-1}) and 1.1 g L^{-1} (0.02 mol L^{-1}) were prepared by dissolving the required amount of salts in 1 M hydrochloric acid solution.

Organic phases. Bis-(2-ethylhexyl)-phosphoric acid (Aldrich, purity = 97%), Cyanex® 272 (Cytec, purity > 85%), Ionquest® 801 (Solvay, purity not specified), Cyanex® 301 GN (Cytec, purity not specified) were used without further purification. Extraction solvents were prepared by diluting the commercial and synthesized extractants in kerosene (Sigma Aldrich, reagent grade, low odour) without phase modifiers as no third-phase formation was observed.

Metal-distribution curves (metal extraction efficiency *vs.* pH)

The extraction properties of the organophosphorus acids towards Co(II), Ni(II) and Mn(II) in acidic chloride media were

Table 1 Yield and purity of the synthesized extractants

No.	Name	Chemical structure	% Yield	% Purity
4a	Bis(1,3-dibutoxypropan-2-yl)phosphoric acid (BiDiBoPP)		78	95
4b	Bis(1,3-diisobutoxypropan-2-yl)phosphoric acid (IPA)		90	94
4c	Bis(5,8,12,15-tetraoxanonadecan-10-yl)phosphoric acid (TPA)		84	92
4d	Bis(undecan-6-yl)phosphoric acid (UPA)		92	90
4e	Bis(1,3-dioctyloxypropan-2-yl)phosphoric acid (OPA)		75	90
4f	Bis(1,3-di-2-ethylhexyloxypropan-2-yl)phosphoric acid (EHPA)		77	92

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evaluated by plotting the metal distribution curves (extraction efficiency %*E vs.* pH). Extraction efficiency was calculated as follows.

$$\%E = 100\frac{[\mathrm{M}]_{\mathrm{org}}V_{\mathrm{org}}}{[\mathrm{M}]_{\mathrm{org}}V_{\mathrm{org}} + [\mathrm{M}]_{\mathrm{aq}}V_{\mathrm{aq}}} = 100\frac{[\mathrm{M}]_{\mathrm{aq,ini}} - [\mathrm{M}]_{\mathrm{aq}}}{[\mathrm{M}]_{\mathrm{aq,ini}}} \quad (8)$$

where the phase volume ratio between the organic and the aqueous phase (V_{org}/V_{aq}) is equal to unity. $[M]_{org}$ and $[M]_{aq}$ denote the metal concentrations at the equilibrium in organic and aqueous phases, respectively. $[M]_{aq,ini}$ represents the initial concentration of metal in aqueous phase.

In order to plot the metal-distribution curves, the pH values of the aqueous phases were adjusted by using NaOH and HCl (standard solution, Alfa Aesar). Batch experiments were conducted at 25 °C in a flask containing equal volumes of aqueous and organic phases (10 mL; $V_{org}/V_{aq} = 1$). The biphasic system was shaken with a Thermoshaker (Gerhardt) at 100 rpm for 15 minutes. Preliminary experiments on the kinetics of extraction of Ni(II), Co(II) and Mn(II) showed that equilibrium was reached in all cases within 5 minutes of contact. After phase separation, the aqueous phase was filtered on nylon filter (VWR, Sartorius®, 0.20 μm) and the equilibrium pH of the aqueous phase was measured. Metal concentrations in aqueous solutions were determined by ICP-OES (ICAP 6000 Series, Thermo Scientific) at 243.7 nm for nickel, 237 nm for cobalt and 257 nm for manganese after diluting the sample in hydrochloric acid (ICP standard solution, 37%, VWR). Metal ion concentration transferred from the aqueous phase into the organic phase was then deduced by mass balance in order to calculate the extraction efficiency defined in eqn (8). Experiments were duplicated and the experimental error on the distribution coefficients of metals was estimated to be within 5%.

Quantitative structure–properties relationships

Quantitative Structure–Activity Relationship (QSAR) and Quantitative Structure–Property Relationship (QSPR) studies are the typical areas of chemical research in which the chemical properties of a compound are related with the structure of molecules represented by the molecular descriptors. The term molecular descriptor indicates a characterization of a molecule by a number (or numbers) that primarily is (are) "*the final result of a logical and mathematical procedure which transforms chemical information encoded within a symbolic representation of a molecule*".[33] QSPR methods were successfully applied for *e.g.* prediction of acidity constants of some anthraquinone derivatives in binary methanol–water systems,[34] octanol–water partition coefficient[35], design of ligands for the separation of lanthanides and actinides[36] or prediction of pK_a for benzoic acids in different solvents.[37] In this paper, the QSPR method for estimating pK_a values of the investigated cationic exchangers was applied. Molecular descriptors were calculated using the Parameter Client software (VCCLAB).[38,39]

The Multiple Linear Regression (MLR) and Partial Least Square (PLS) analyses were performed using MATLAB and Statistics Toolbox (Release 2010b, The MathWorks, Inc., Natick, Massachusetts, USA) as well as PS Imago 3 (IBM SPSS Statistics 23, IBM Corporation, Armonk, NY, USA) software. The stepwise procedure in MLR was applied to remove the insignificant coefficients from the regression model. Alternatively, the optimum number of descriptors (among 1309 calculated) in MLR was selected according to the procedure described in ref. 40. Statistical validity of the correlation was estimated using the values of determination coefficient (R^2) and test function F of Snedecor–Fisher (F-statistics). In order to evaluate the predictive accuracy of the model, the cross-validation procedure was applied.

Results and discussion

As mentioned previously, metal extraction properties of extracting agents are related to the thermodynamic parameters such as pK_a value (eqn (7)). The present section investigates the extraction properties of six new and four commercial cationic exchangers. These properties are analysed in the light of pK_a deduced from QSPR model since no pK_a values are available in the literature for the six new molecules.

QSPR model for determining pK_a values

In order to perform QSPR calculations for evaluating pK_a values of the investigated cationic exchangers, two different training data sets were applied. In the first part of the study, a training data set of 55 dissociation constants was used (see ESI,† data set I = molecules from 1 to 55). The set of data was carefully selected from experimental data reported in literature by potentiometric titration in water. In particular, we paid attention to select pK_a values determined under very close experimental conditions in terms of media, ionic strength, temperature, *etc.* This database and the corresponding references are reported in ESI.†

The calculated molecular descriptors (1309 MDs) for these compounds were linearly correlated with the dissociation constants. After performing the regression analysis with the forward variable selection method (to remove the insignificant coefficient from the regression model), the following relationship was obtained:

$$\mathrm{p}K_{\mathrm{a}} = 0.910(0.037)\mathrm{Jhetv} - 10.8(2.7)\mathrm{R4p} + - 1.18(0.18)\mathrm{MATS2v} + 4.05(0.78)\mathrm{RBF} \quad (9)$$

$$R^2 = 0.989,\ \mathrm{S.D.} = 0.28,\ F = 1114,\ N = 55,\ Q_{\mathrm{cv}}{}^2 = 0.921$$

where Jhetv denotes the Balaban-type index calculated from van der Waals weighted distance matrix, R4p+ corresponds to the R maximum autocorrelation of the lag 4 (weighted by atomic polarizabilities) index, MATS2v is the Moran autocorrelation for the lag 2 (weighted by atomic van der Waals volumes) index, and RBF represents the rotatable bond fraction descriptor. Eqn (9) was used to predict the dissociation constants (Table 2, Model 1). The PLS method with 5 latent variables for the training data set I was also applied to calculate pK_a values (Table 2, Model 2). The highest validation coefficient ($Q_{cv}{}^2 = 0.854$) was obtained when the determination

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Table 2 Experimental pK_a values of a set of organophosphorus extractants and corresponding calculates pK_a values by means of the QSPR models developed in the present work. M_i = Model i

No.	Acid	pK_a values				
		Exp.	M1	M2	M3	M4
1	Cyanex 301 $C_5H_{10}(C_2H_5)CH_2$–	2.80	—	—	—	—
2	Cyanex 272 $C_5H_{10}(C_2H_5)CH_2$–	3.73	4.17	3.91	3.85	3.72
3	Ionquest 801 $C_5H_{10}(C_2H_5)CH_2$–$C_5H_{10}(C_2H_5)CH_2O$–	3.3	3.26	3.37	3.5	3.33
4	D2EHPA $C_5H_{10}(C_2H_5)CH_2O$–	2.75	2.3	2.59	2.71	2.76
5	BiDiBOPP $(C_4H_9OCH_2)_2CHO$–	—	3.58	4.04	1.65	2.35
6	IPA $(i\text{-}C_4H_9OCH_2)_2CHO$–	—	3.43	4.24	2.43	2.42
7	TPA $(C_4H_9OC_2H_4OCH_2)_2CHO$–	—	4.01	5.53	1.80	1.66
8	UPA $(C_5H_{11})_2CHO$–	—	2.99	3.45	2.88	2.85
9	OPA $(C_8H_{17}OCH_2)_2CHO$–	—	3.83	5.65	2.09	3.07
10	EHPA $(C_4H_9CH(C_2H_5)CH_2OCH_2)_2CHO$–	—	3.98	6.90	3.79	4.02

coefficient is equal to 0.958. The selected substances used for performing QSPR calculations in Models 2 and 3 are the analogues of phosphoric (or phosphinic) acids and only 36 extractants (from among 55) are alkyl substituents which are similar to the synthesized cationic exchangers. Therefore, the PLS and MLR methods were afterward applied to the data set of 36 extractants (phosphoric and phosphinic acids with alkyl substituents only) [data set II: molecules from 1 to 36]. The following MLR with 5 parameters from 1271 descriptors was deduced (eqn (10)):

$$\begin{aligned} pK_a = &-22.9(1.6) + 0.910(0.45)\text{BEHp1} + 0.181(0.030)\text{C-003} \\ &- 0.429(0.074)\text{Mor15e} + 0.53(0.14)\text{MATS2m} \\ &+ 0.213(0.054)\text{Jhetp} \end{aligned} \tag{10}$$

$$R^2 = 0.984,\ \text{S.D.} = 0.12,\ F = 377,\ N = 36,\ Q_{cv}^2 = 0.978$$

where BEHp1 denotes the highest eigenvalue *n*. 1 of Burden matrix (weighted by atomic polarizabilities), MATS2m is the Moran autocorrelation of lag 2 (weighted by atomic masses), Mor15e – 3D-MoRSE represents the signal 15 (weighted by atomic Sanderson electronegativities) index, Jhetp is the Balaban-type index from polarizability weighted distance matrix, and C-003 denotes CHR3 atom-centred fragments.

In the PLS model analysis the highest cross-validation coefficient ($Q_{cv}^2 = 0.928$) was obtained for 9 latent variables, with the determination coefficient (R^2) equals to 0.998.

The calculated pK_a values by means of the MLR and PLS methods are reported in Table 2 (Models 3 and 4, respectively).

The calculated pK_a values are quite different from one model to another. The pK_a values estimated by Models 3 and 4 are in the best accordance with experimental values of pK_a of Cyanex 272, D2EHPA and Ionquest 801 (Table 2). Furthermore, it is worth noting that the pK_a values calculated with these models follow the same general trends as in the literature (see ESI†), *i.e.* an increase of the number of oxygen atoms in the hydrophobic chains of organophosphorus acids leads to a decrease of pK_a values due to attractive inductive effects (extractants 4 and 7 in Table 2).

Model 3 predicts that the pK_a values of the extractants 4 and 5 are different while their chemical structures are very close. The difference between these two molecules arises only for the branching of the hydrophobic chains. Conversely, Model 4 predicts branching does not influence significantly the pK_a values of extractants 4 and 5. Therefore, models 4 seems to be more relevant to calculate pK_a values since it was expected that branching in the hydrophobic chains may influence pK_a values very slightly.

Extraction properties of new cationic exchangers

Fig. 1 shows the extraction efficiencies of Co(II), Ni(II) and Mn(II) *vs.* pH for Cyanex 301, Cyanex 272, Ionquest 801 and D2EHPA as well as for the 6 new cationic exchangers synthesized in the laboratory (see Table 2). The pH values at half extraction (pH for which 50% of metals are extracted, $pH_{1/2}$) are reported in Table 3. All investigated extracting agents can recover Ni(II), Mn(II) and Co(II) from acidic chloride solution. In certain cases, the extraction efficiency is not equal to zero under very acidic conditions likely because of the presence of impurities, which can extract metals even at very low pH because impurities might be solvating agents (extraction efficiency of metals by solvating agents does not depend on pH).

The value of $pH_{1/2}$ can be derived from eqn (7) as follows:

$$pH_{1/2} = pK_a - \tfrac{1}{2}(\log K_{D,ML_2} + \log \beta + \log(\nu) - \log[\{HL\}_{org}]) \tag{11}$$

where ν represents the phase volume ratio between organic and aqueous phases (V_{org}/V_{aq}).

This equation shows that $pH_{1/2}$ values are influenced by (i) the hydrophobicity of the cationic exchanger (an increase of the hydrophobicity, *i.e.* an increase of K_{D,ML_2}, is responsible for a decrease of $pH_{1/2}$), (ii) the pK_a values (a decrease of pK_a is responsible for a decrease of $pH_{1/2}$) and (iii) the affinity of the cationic exchanger towards metals (an increase of β is responsible for a decrease of $pH_{1/2}$). Therefore, it is expected that alkyl chain branching at the vicinity of the acidic group is responsible for a decrease of β due to steric hindrance, and thus, an increase of $pH_{1/2}$. Likewise, the presence of oxygen or sulphur atoms in the acidic group of the extracting agents may change β (as

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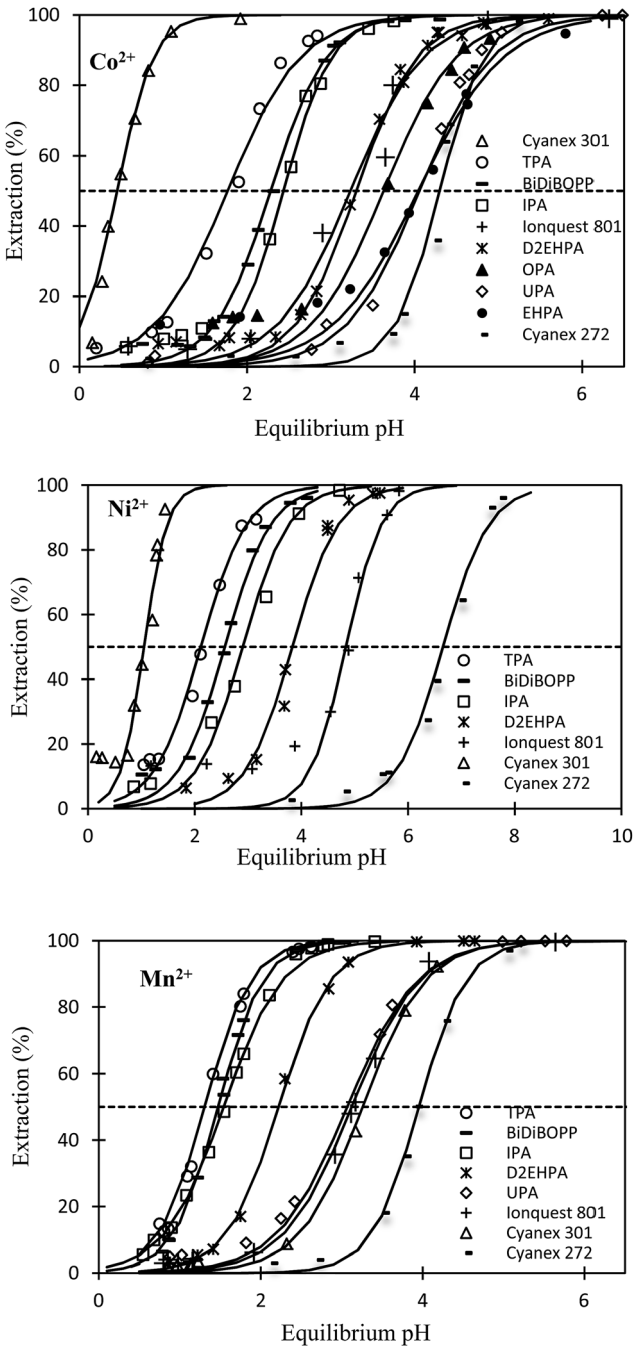

Fig. 1 Extraction efficiency (%E) of Ni(II), Co(II) and Mn(II) by the cationic exchangers diluted in kerosene as a function of equilibrium pH. Temperature = 25 °C; phase volume ratio V_{org}/V_{aq} = 1; chloride concentration = 1 M.

predicted by the Hard–Soft–Acid–Base Theory) and consequently, the value of $pH_{1/2}$.

Such influences of branching, hydrophobicity of the alkyl chains and the presence of oxygen or sulphur atoms in the acidic function of the cationic exchangers have been studied in the present paper by investigating the extraction properties of several cationic exchangers (Fig. 2).

Table 3 shows pK_a and $pH_{1/2}$ values increase as follows:

Table 3 Calculated and experimental pK_a values of cationic exchangers and pH at half extraction towards Mn(II), Co(II) and Ni(II) ($pH_{1/2}$)

		pK_a		$pH_{1/2}$		
No.	Name	Exp.	Calc.	Mn(II)	Co(II)	Ni(II)
1	Cyanex 301	2.80	—	3.2	0.5	1.0
2	Cyanex 272	3.73	3.72	3.9	4.3	6.6
3	Ionquest 801	3.30	3.33	3.1	3.2	4.8
4	D2EHPA	2.75	2.76	2.2	3.3	3.8
5	BiDiBOPP	—	2.35	1.5	2.3	2.6
6	IPA	—	2.42	1.5	2.4	2.9
7	TPA	—	1.66	1.3	2.0	2.1
8	UPA	—	2.85	3.0	4.0	—
9	OPA	—	3.07	—	3.6	—
10	EHPA	—	4.02	—	4.0	—

- pK_a: TPA < BiDiBOPP ≤ IPA < D2EHPA ≤ UPA < OPA < Ionquest 801 < Cyanex 272 < EHPA.

- $pH_{1/2}$ for Mn(II): TPA ≤ BiDiBOPP = IPA < D2EHPA < UPA ≤ Ionquest 801 < Cyanex 301 < Cyanex 272.

- $pH_{1/2}$ for Co(II): Cyanex 301 ≪ TPA < BiDiBOPP ≤ IPA ≪ Ionquest 801 ≤ D2EHPA < OPA < UPA = EHPA < Cyanex 272.

- $pH_{1/2}$ for Ni(II): Cyanex 301 < TPA < BiDiBOPP < IPA < D2EHPA < Ionquest 801 < Cyanex 272.

It is interesting to notice that Mn(II) extraction from acidic chloride media by the investigated cationic exchangers is mainly governed by the pK_a probably because the sum of log β and log K_{D,ML_2} does not vary so much from a cationic exchanger to another one (the variation of β may compensate the variation of K_{D,ML_2}). Therefore, more the cationic exchanger is

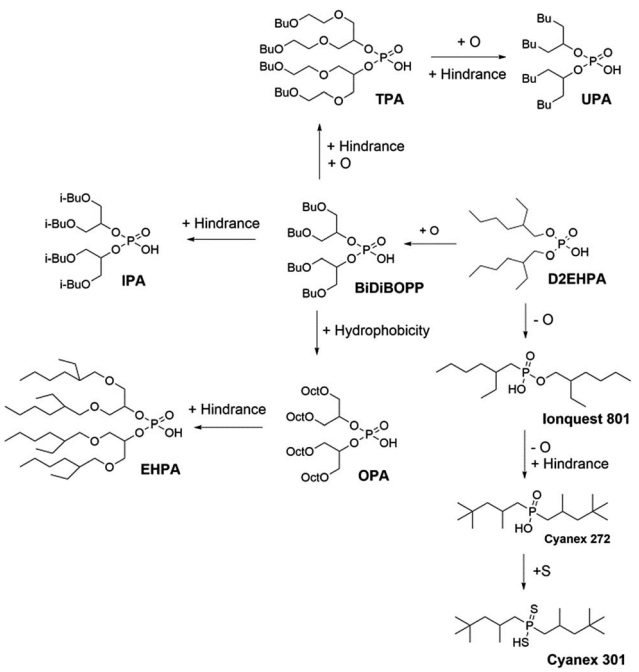

Fig. 2 Changes in the chemical structures of the synthesized cationic exchangers.

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hydrophobic, more the affinity between Mn(II) and the cationic exchanger is weakened and log β + log K_{D,ML_2} remains close to zero (see eqn (12)).

Regarding Ni(II) and Co(II) extraction, the behaviour of these two metals is similar as $pH_{1/2}$ values vary in the same order. This is not surprising as these two metals are known to have the same behaviour in solvent extraction. However, the trend is completely different for Ni(II) and Co(II) compared to Mn(II) as $pH_{1/2}$ values do not follow the variation of pK_a. Therefore, unlike Mn(II), the sum of log β and log K_{D,ML_2} is not the same from a cationic extractant to another one. In particular, it is interesting to notice that Cyanex 301 exhibits the lowest $pH_{1/2}$ (for Ni and Co) whereas its pK_a value is not very low, *i.e.* $pK_a = 2.80$ given that all investigated cationic exchangers exhibit pK_a values between 1.6 and 4.0. The low value of $pH_{1/2}$ can be explained by the presence of sulphur atoms instead of oxygen atoms in the complexing group (Cyanex 301 and Cyanex 272 have the same alkyl chains). These results are in agreement with the Hard–Soft–Acid–Base theory (HSAB), which indicates that soft atoms such as sulphur have more affinity with soft acids or borderline hard acids like Ni(II) and Co(II) rather than with hard acids like Mn(II). Therefore, the value of β may be much greater than the value of pK_a, resulting in low value of $pH_{1/2}$ for Co(II) and Ni(II) extraction by Cyanex 301.

Despite the high pK_a value of EHPA, $pH_{1/2}$ is not so high likely because EHPA–metal complexes exhibit low value of β due to steric hindrance and high value of K_{D,ML_2} resulting from the presence of long alkyl chains in the chemical structure of EHPA.

More generally, the presence of oxygen atoms in the hydrophobic chains of the cationic exchangers decreases the $pH_{1/2}$ values. Unfortunately, oxygen atoms in the hydrophobic chains are also responsible for a decrease of the selectivity (the difference in $pH_{1/2}$ between Ni(II), Co(II) and Mn(II) for the same cationic exchanger is lowered when oxygen atoms are inserted in the hydrophobic chains as illustrated in Table 3). Likewise, steric hindrance may play a negative role by disfavouring the metal–ligand interactions leading to an increase of the $pH_{1/2}$ values provided that the steric hindrance factor would be more important than the hydrophobic factor.

Comparison of $pH_{1/2}$ values of the cationic exchangers for the extraction of Co(II), Ni(II) and Mn(II) shows the decrease of $pH_{1/2}$ is accompanied by a loss in selectivity, which gets difficult Co–Ni–Mn separation (Table 3). For instance, TPA exhibits the lowest $pH_{1/2}$ values (1.3–2.1) but the difference in $pH_{1/2}$ is too low for allowing efficient Ni–Mn–Co separation. As a sake of illustration, Fig. 3 shows extraction curves *vs.* pH of Co(II), Ni(II) and Mn(II) from acidic chloride media by using TPA and IPA in kerosene (these two extractants are the most interesting molecules among those synthesized in the present paper). The acidic chloride solutions containing Co(II), Ni(II) and Mn(II) simulate leaching solutions of cathode from spent lithium-ion batteries ($Li_{1/3}Ni_{1/3}Mn_{1/3}O_2$) or leaching solution of sea nodules.[1,41–43] Mn(II) can be easily separated towards Ni(II) and Co(II) by controlling the pH of simulated leaching solutions of cathodes at 1.1 (Fig. 3a) and 1.6 (Fig. 3c) when the extractant is TPA and IPA, respectively. Less than 10% of Ni(II) and Co(II) are co-extracted but the use of multi-stage solvent extraction

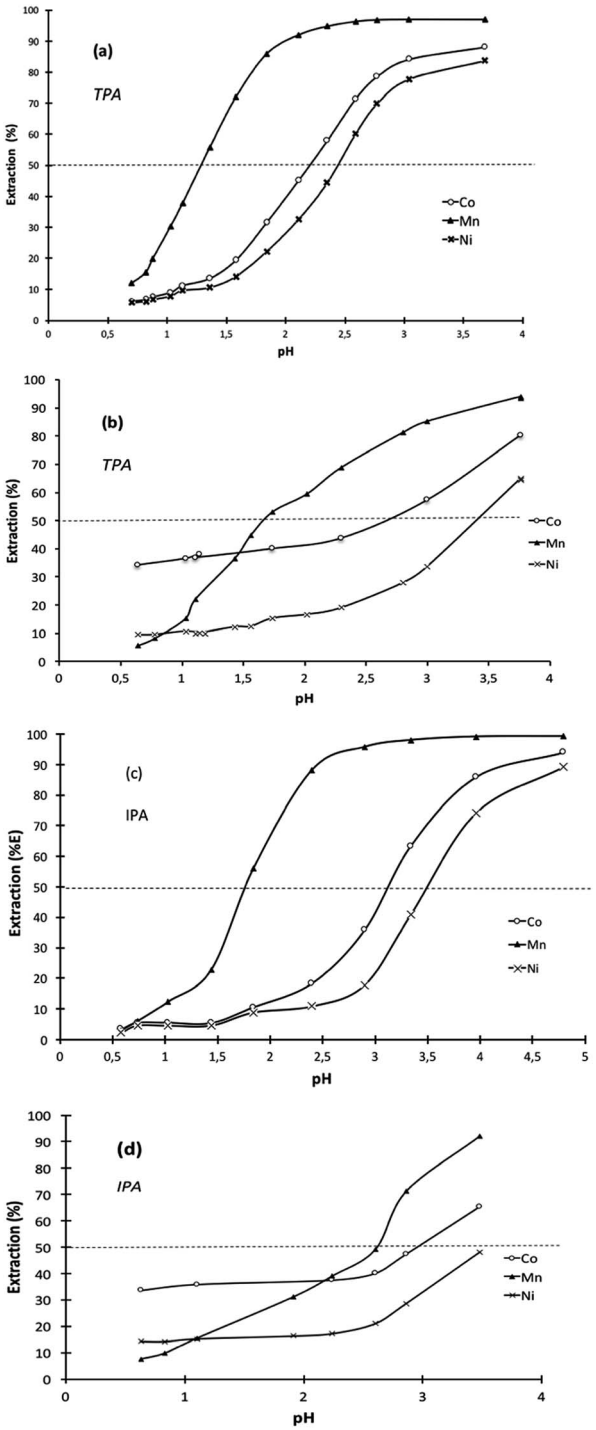

Fig. 3 Extraction efficiency (%*E*) of Ni(II), Co(II) and Mn(II) by 0.25 M TPA (graphics (a) and (b)) or IPA (graphics (c) and (d)) diluted in kerosene as a function of pH at equilibrium. Temperature = 25 °C; phase volume ratio $V_{org}/V_{aq} = 1$; aqueous phase = (a) and (c): [Co] = [Ni] = [Mn] = 0.016 mol L^{-1} (typical composition of leaching solution of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode from spent Li-ion batteries); (b) and (d) [Co] = 3.0×10^{-4} mol L^{-1}, [Ni] = 8.0×10^{-2} mol L^{-1}, [Mn] = 3.7×10^{-4} mol L^{-1} (typical composition of leaching solution from sea nodule) in 1 M chloride solution.

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equipment such as mixers-settlers will permit full separation of Mn(II) towards Co(II) and Ni(II). However, separation of Co(II) and Ni(II) cannot be achieved by using TPA or IPA as $pH_{1/2}$ values are too close. Change in composition of the aqueous solution affects strongly the metal separation. For instance, the ability of TPA or IPA to separate Mn(II) towards Co(II) and Ni(II) is strongly reduced when the extraction solvent is contacted with an aqueous phase simulating a leaching solution of sea nodules instead of a leaching solution of cathodes from spent lithium-ion batteries (Fig. 3b and d). The high Co(II) extraction at low pH might be due to the presence of 6% and 8% of impurities in IPA and TPA, respectively. These impurities are likely solvating agents because such molecules can extract metals even at low pH. The high affinity of the impurities for Co(II) and the low Co(II) concentration in aqueous phase, like in the case of leaching solutions of cathodes, exalts Co(II) extraction efficiency and no selectivity can be achieved even at low pH values.

Conclusion

The $pH_{1/2}$ values of the metal distribution curves for cationic exchangers depends on the hydrophobicity of the cationic exchanger (an increase of the hydrophobicity, *i.e.* an increase of the distribution constant between the organic and the aqueous phase is responsible for a decrease of $pH_{1/2}$), the pK_a value of the cationic exchanger (a decrease of pK_a is responsible for a decrease of $pH_{1/2}$) and the affinity of the cationic exchanger towards metals (an increase of the complexation constant is responsible for a decrease of $pH_{1/2}$).

In the case of Ni(II) and Co(II) extraction, the $pH_{1/2}$ follows the variation of pK_a unlike Mn(II). For the latter, it appears that the more hydrophobic the cationic exchanger is, the more weakened the affinity between Mn(II) and the cationic exchanger is. Furthermore, the presence of oxygen atoms in the hydrophobic chains of the cationic exchangers decreases the $pH_{1/2}$ values and reduces the selectivity in Co–Ni–Mn extraction. Obviously, the nature of the atoms in the complexing group influences the extraction properties in accordance with the Hard–Soft–Acid–Base theory (HSAB). More generally, it appears that a decrease of pK_a values of organophosphorus cationic exchangers by adding oxygen atoms in the hydrophobic chains is responsible for an important loss of selectivity towards cobalt, nickel and manganese.

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