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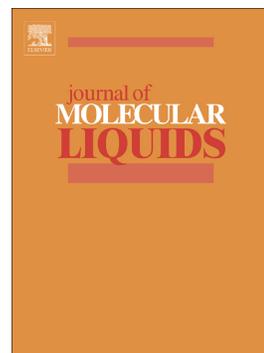


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Investigation of aggregation and acid dissociation of new cationic exchangers for liquid-liquid extraction

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Abstract

Potentiometric titration and Vapour Pressure Osmometry were used to characterise the acidic properties in an acidic chloride solution and the aggregation behaviour in *n*-heptane of a series of four extractants synthesized in the present work and derived from bis-(2-ethyl-hexyl-phosphoric) acid, a commercial extractant noted D2EHPA. Four other commercial organophosphorus extractants (D2EHPA, Cyanex 272, Cyanex301, Ionquest 801) were also characterized by these techniques. Their hydrophobicity was also investigated by determining the partition coefficient of the monomeric form between an acidic chloride solution and *n*-dodecane. The *pka* values, the dimerization and trimerisation constants were deduced from experimental results by means of appropriate physicochemical models.

Keywords: Acidic dissociation constant; cationic exchanger; dimerisation; physicochemistry; trimerisation; solvent extraction.

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1. INTRODUCTION

Solvent extraction is a mature technology that is used in industry for the recovery of metals from leaching solutions. In solvent extraction, the aqueous leaching solution is contacted with an organic phase containing an extractant or a mixture of extractants diluted in an aliphatic or an aromatic diluent. Both immiscible phases are mixed and settled in mixers-settlers. Afterwards, metals in the loaded organic phase are stripped with an appropriate aqueous solution before performing further treatments such as precipitation/crystallisation or electrolysis.

Extractants used in solvent extraction are divided into three families: (i) cationic exchangers such as bis-(2-ethylhexyl)phosphoric acid (D2EHPA), bis-(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), etc., (ii) anionic exchangers such as tri-n-octylamine (Alamine® 336), Trioctylmethylammonium chloride (Aliquat® 336), etc. and (iii) solvating agents such as tri-n-octylphosphine oxide (TOPO), tri-n-butylphosphate (TBP), etc. [1]. The choice of the solvent depends on the nature of the leaching solution, the nature of the metals to be extracted and the nature of the impurities present in the leaching solution. The search for new extractants is a real challenge in the development of liquid-liquid extraction processes since it is mandatory to treat more and more complex ores or secondary resources in an efficient and economical way. Cationic exchangers are used in many applications such as the recovery of cobalt from acidic sulfate or chloride media [2-4], uranium from concentrated phosphoric acid [5, 6], etc.

Although solvent extraction seems easy to implement, its physicochemistry is complex because the system contains two phases in which many equilibria occur as well as an interphase. Furthermore, the non-ideal behaviour of the system due to high concentration in aqueous phase also increases the complexity of the physicochemistry of liquid-liquid extraction.

In solvent extraction chemistry, the knowledge of the acidity constants and the interaction constants between the components of an extracting system is essential to clarify processes occurring in solution and to ascertain the stoichiometry of the extracted species [7, 8]. In this paper, the physicochemical properties of new synthesized and commercial organophosphorus cationic exchangers have been investigated (Table 1). These extractants could be used for the recovery of cobalt, nickel, and manganese from acidic sulfate or chloride media. They were also studied for the recovery of uranium from concentrated phosphoric acid providing that they are used in mixture of solvating agents such as tri-n-octylphosphine or tri-n-

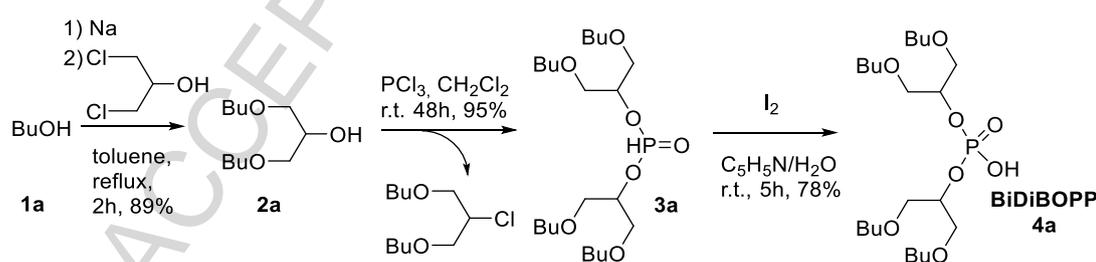
butylphosphate. The use of these extractants instead of more classical ones such as D2EHPA or Cyanex 272 may be beneficial since the addition of oxygen atoms in the hydrophobic chains could advantageously lead to a decrease of the pK_a values, and therefore an increase of metal extraction efficiency at low pH, while the increase of the steric hindrance of the molecule may improve the selectivity of the extractants and improve metal separation in solvent extraction processes. In particular, aggregation behaviour and acidic dissociation of the molecules have been determined by means of potentiometric and vapour pressure osmometry (VPO) measurements combined with appropriate models.

2. Material and Methods

2.1. 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 $\geq 99.8\%$), ethylene glycol butyl ether (Sigma Aldrich, purity $\geq 99\%$), 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. [6] (Scheme 1).



Scheme 1

The 1,3-dibutoxy-2-propanol (**2a**) was synthesized by the 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**) with 78% yield. After purification, **3a** was oxidised by I_2 in pyridine-water mixture with ratio of 9:1 to form bis(1,3-dibutoxypropan-2-yl) phosphoric acid (BiDiBOPP, **4a**) (Scheme 1).

D2EHPA (Sigma Aldrich, purity 97%), Cyanex 272 (Solvay, purity=85%), Cyanex 301 (Solvay, purity 90%), Ionquest 801 (Solvay, purity 96%) were used as delivered. Potassium chloride, ethanol, 2-propanol and other reagents were of analytical reagent grade.

The values of pK_a in water/2-propanol mixtures were determined by potentiometric titrations with a glass electrode (Metrohm® 913) at 25 °C under nitrogen atmosphere (inert conditions). It was not possible to use water-ethanol mixtures due to solubility issues of the extracting agents synthesized in the present work. During the potentiometric titrations, the ionic strength of the water/propan-2-ol mixtures was kept constant at 0.1 mol.L⁻¹ by using KCl.

The electrode calibration was performed in buffer solutions containing different concentrations of 2-propanol in water according to the procedure described by Wilson et al. and Mussini et al. [11, 12]. As the literature reported only buffer solutions in water/ethanol mixtures, it was assumed that pH values of the buffer solutions in water/2-propanol mixtures were the same as those in water/ethanol solutions reported in Table 5. Such an assumption relies on the fact that the chemical structures of ethanol and 2-propanol are similar, the same types of interactions occurs in water/ethanol and water/2-propanol mixtures and these solvents exhibit similar values of dielectric constants (20.2 and 25.2 at 20 °C for 2-propanol and ethanol, respectively) and the same dipolar moments (1.69 D). This assumption was checked by determining the pK_a of D2EHPA in water-ethanol and water-2-propanol mixtures by potentiometric measurement assuming that water/2-propanol buffer solutions have the same pH as water/ethanol buffer solutions reported in Table 5. Similar values of pK_a of D2EHPA in water were deduced from potentiometric measurements in water/ethanol and water/2-propanol media, i.e $pK_a=2.3$ and 2.6, respectively. Although a difference is observed between both pK_a values, it has been considered in the present paper that the difference is sufficiently small given the large discrepancies of pK_a reported in the literature [See supporting information of ref. 3].

2.3. *Measurement of phosphorus content in aqueous phases*

Solubility of organophosphorus compounds in aqueous phase was determined by the colorimetric method after digestion with concentrated sulphuric acid as reported by Biswas et al. [14]. In this method, orthophosphate was formed, during the digestion of the organophosphorus compounds. Orthophosphate concentration was estimated by the molybdenum-blue method at 830 nm [15].

2.4. *Vapor Pressure Osmometry measurements*

The organic solutions of tri-n-octylamine (TOA, Aldrich, purity=99%) and organophosphorus acids diluted in n-heptane were prepared by weight so that extractant concentrations were comprised between 0.05 and 0.5 mol kg⁻¹. Vapor Pressure Osmometry (VPO) measurements were carried out at 25 °C using a Knauer K-7000 Vapour Pressure Osmometer.

Prior to VPO measurements, the thermocouple head was cleaned thoroughly, and the osmometer was calibrated with TOA diluted in n-heptane. Calibration was performed using TOA diluted in n-heptane because TOA was expected to be monomeric in n-heptane in the concentration range of interest.

The difference of resistance (ΔR) was measured as a function of the concentration for both standard and organophosphorus acids. The measured property ΔR may be expressed as a function of the total extractant concentration m_{HL}^0 as:

$$\Delta R = k_{cal} m_{HL}^0 \quad (1)$$

where k_{cal} is the calibration constant, which can be obtained by measuring ΔR for different TOA solutions since TOA exists only as monomers in n-heptane in the range of investigated concentrations. In order to obtain reliable ΔR values, the drop size was kept as constant as possible and equal in both thermistors, and the measurements were performed by reading ΔR five minutes after placing the drops on the thermistors. Five readings were recorded for each sample and the average value was used in all calculations. In this manner, the precision of ΔR were maintained below 2%. The calibration constant deduced from VPO measurements with TOA in n-heptane at 25 °C was $k_{cal}=2015,5 \Omega.kg.mol^{-1}$.

3. Results and Discussions

3.1. Acid dissociation constants

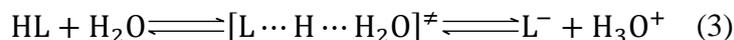
The low water solubility of long chain organophosphorus acids prevents the direct determination of pK_a in water by potentiometric measurements. Therefore, the acid dissociation constants of the organophosphorus acids were determined by potentiometry in water/propan-2-ol mixtures. The pK_a values of the organophosphorus compounds in water/propan-2-ol mixtures were determined by using the Gran equation:

$$V_b \cdot 10^{-pH} = \frac{\gamma_{HL}}{\gamma_{L^-}} K_a (V_e - V_b) \quad (2)$$

where V_b is the volume of sodium hydroxide used for the titrations, γ_{HL} and γ_{L^-} are the activity coefficients of the protonated form (HL) and the dissociated form (L⁻) of the

organophosphorus compounds, respectively. K_a denotes the acid dissociation constant and V_e is the equivalence volume. It is expected that the ratio $\frac{\gamma_{HA}}{\gamma_{A^-}}=1$ at constant ionic strength.

Acid dissociation can be described by the following equilibrium [16]:



where $[\text{L} \cdots \text{H} \cdots \text{H}_2\text{O}]^\ddagger$ is an activated complex.

The solvent effect of ion-ion, ion-dipole and dipole-dipole interactions can be estimated by means of the Kirkwood equation [17, 18]:

$$pK_a = pK_a^0 + \frac{1}{2,303} \left[\frac{e^2}{2kT} \left(\frac{1}{r_{L^-}} + \frac{1}{r_{\text{H}_3\text{O}^+}} \right) + \frac{3}{4kT} \left(\frac{\mu_\ddagger^2}{r_\ddagger^3} - \frac{\mu_{\text{HL}}^2}{r_{\text{HL}}^3} - \frac{\mu_{\text{H}_2\text{O}}^2}{r_{\text{H}_2\text{O}}^3} \right) \right] \frac{1}{\varepsilon} \quad (4)$$

where ε is the dielectric constant of the solvent, pK_a^0 is the pK_a value at infinite dielectric constant, e is equal to $1.6 \cdot 10^{-19}$ C, k is the Boltzmann constant ($1.38 \cdot 10^{-23}$ m² kg s⁻² K⁻¹), T is the temperature in Kelvin, r is the radius of charges species (in m), μ is the dipole moment (in D).

This equation shows a linear relationship between pK_a values and $1/\varepsilon$. Such a relationship is interesting as it allows the determination by extrapolation of pK_a of compounds poorly soluble in water by using solvent mixtures in which the compound is soluble. In the present case, mixtures of water and propan-2-ol was utilized since the synthesized and commercial organophosphorus compounds exhibit a very low solubility in water and high solubility in water/propan-2-ol mixtures.

In order to calculate the pK_a values of the organophosphorus compounds in water, their pK_a in several mixtures of water and propan-2-ol have been determined by potentiometric measurements and the Gran method [Eq. (2)]. Figure 1 demonstrates the validity of Eq. (4).

In Figure 1, the values of the dielectric constants of the water/propan-2-ol mixtures have been calculated by using Eq. (5) deduced from the Redlich-Kister equation [19] and the data reported by Hasted [20]:

$$\varepsilon_{w/\text{prop}} = x_{\text{prop}} \varepsilon_{\text{prop}} + (1-x_{\text{prop}}) \varepsilon_w [34.809(1-2x_{\text{prop}})^4 + 7.0591(1-2x_{\text{prop}})^3 + 3.3614(1-2x_{\text{prop}})^2 - 54.456(1-2x_{\text{prop}}) - 94.878] \quad (5)$$

where $\varepsilon_{w/\text{prop}}$, ε_w and $\varepsilon_{\text{prop}}$ are the dielectric constants of the water-ethanol mixture, water ($\varepsilon_w=78.5$) and 2-propanol ($\varepsilon_w=18.6$), respectively, and x_{prop} denotes the mole fraction of 2-propanol in the mixture.

Table 6 gathers the pK_a values of the organophosphorus acids in aqueous solution of 1 mol.L^{-1} KCl deduced by extrapolation at $\epsilon_r=78.5$ (dielectric constant of water at $25 \text{ }^\circ\text{C}$) with the linear relationship found in Figure 1.

The pK_a values determined in the present work for the commercial extractants are in accordance with those reported in the literature (Table 6). The difference in pK_a is likely due to the difference in ionic strength and experimental methods used to determine the pK_a (examination of pK_a data from the literature shows discrepancies depending on the methods used for determining pK_a of hydrophobic compounds [21]).

It can be observed in Table 6 that an increase of the number of oxygen atoms in the hydrophobic chains and an increase of the number of P-O bonds in the structure of the organophosphorus acids decrease pK_a values likely due to attractive inductive effects, which are responsible for an increase of O-H bond polarization. Such an observation was also reported by Fu et al. and Binghua et al. [22, 23]. Furthermore, there is no influence of the nature of the hydrophobic chains on the pK_a values, excepting for BiDiBOPP and IPA. In the latter cases, branching of the hydrophobic chains is responsible for a slight increase of pK_a as it has ever been reported by Martinez et al. [24]. Furthermore, the acidity increases when an oxygen atom is replaced by a sulphur atom because of an increase of the proton lability in the presence of sulphur atom resulting from the difference in electronegativity [25].

3.2. Aggregation constants

Figure 2 shows ΔR deduced from VPO measurements as a function of the total concentration of the organophosphorus acids at $25 \text{ }^\circ\text{C}$ [Eq. (1)]. The average molecular weight in g.mol^{-1} of the extractants can be deduced by the following equation:

$$\bar{M} = \frac{k_{cal}}{k_{extractant}} \quad (6)$$

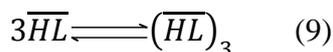
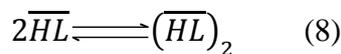
where k_{cal} is the calibration constant ($k_{cal}=2015,5 \text{ } \Omega.\text{kg.mol}^{-1}$ for TOA diluted in n-heptane) and $k_{extractant}$ in $\Omega.\text{kg.g}^{-1}$ is the slope of the linear relationship $\Delta R = k_{extractant} m_{HL}^0$ plotted in Figure 2 where m_{HL}^0 is the total concentration of organophosphorus acid in n-heptane. The values of $k_{extractant}$ and \bar{M} are given in Table 7 as well as the average number of aggregates of the organophosphorus acids, which were calculated by using Eq. (7).

$$\bar{n} = \frac{\bar{M}}{M_{monomer}} \quad (7)$$

where $M_{monomer}$ is the molecular weight of the monomeric forms of organophosphorus acids.

Table 7 shows that the synthesized organophosphorus acids exhibit a weak tendency to form aggregates under the present experimental conditions. However, the organophosphorus acids seem to exist as dimers and they could eventually form trimers.

The aggregation of the organophosphorus acid compounds can be expressed as:



Assuming ideal behavior of organophosphorus acids, the stoichiometric constant K_2 and K_3 for the dimerization and the trimerisation equilibria, respectively, can be written as:

$$K_2 = \frac{m_{(\overline{HL})_2}}{m_{\overline{HL}}^2} \quad (10)$$

and

$$K_3 = \frac{m_{(\overline{HL})_3}}{m_{\overline{HL}}^3} \quad (11)$$

The total concentration of the monomeric form of organophosphorus acid ($m_{\overline{HL}}^0$) can be expressed as:

$$m_{\overline{HL}}^0 = m_{\overline{HL}} + 2K_2 m_{\overline{HL}}^2 + 3K_3 m_{\overline{HL}}^3 \quad (12)$$

The apparent concentration of organophosphorus acid ($m_{\overline{HL}}^{\text{app}}$), i.e. the total concentration of monomeric and associated organophosphorus acids, is defined as:

$$m_{\overline{HL}}^{\text{app}} = m_{\overline{HL}} + K_2 m_{\overline{HL}}^2 + K_3 m_{\overline{HL}}^3 \quad (13)$$

The following equation is deduced from Eq. (13);

$$\frac{dm_{\overline{HL}}^{\text{app}}}{dm_{\overline{HL}}} = 1 + 2K_2 m_{\overline{HL}} + 3K_3 m_{\overline{HL}}^2 \quad (14)$$

By combining Eqs. (12) and (14), the following equation can be written:

$$\frac{dm_{\overline{HL}}^{\text{app}}}{dm_{\overline{HL}}} = 1 + 2K_2 m_{\overline{HL}} + 3K_3 m_{\overline{HL}}^2 = \frac{m_{\overline{HL}}^0}{m_{\overline{HL}}} \quad (15)$$

The average number of aggregates \bar{n} given in Eq. 8 can be rewritten as:

$$\bar{n} = \frac{m_{HL}^0}{m_{HL}^{app}} \quad (16)$$

Therefore, Eq. (15) can be rewritten as follows:

$$\frac{dm_{HL}^{app}}{dm_{HL}} = \bar{n} \frac{m_{HL}^{app}}{m_{HL}} \quad (17)$$

The following expression deduced from Eq. (17) can be used to calculate the concentration of the monomeric form of the organophosphorus acid (m_{HL}):

$$\ln(m_{HL}) - \ln(m_{HL}^0) = \int_{m_{HL}^0}^{m_{HL}^{app}} \frac{1}{\bar{n}} d(\ln(m_{HL}^{app})) \quad (18)$$

with

$$m_{HL}^0 = \frac{w(\text{extractant}) \cdot 1000}{w(\text{solvent}) \cdot MW(\text{extractant})}$$

$$m_{HL}^{app} = \frac{\Delta R}{k_{cal}}$$

where $w(\text{extractant})$ and $w(\text{solvent})$ are the weight of extractant and solvent, respectively, and MW is the molecular weight of the extractant in $\text{g}\cdot\text{mol}^{-1}$. ΔR and k_{cal} denote the difference in resistance and the calibration constant in $\Omega\cdot\text{kg}\cdot\text{mol}^{-1}$ measured during VPO experiments, respectively.

Finally, the dimerization and trimerisation constants can be calculated by plotting the following equations:

$$\frac{\frac{m_{HL}^0}{m_{HL}} - 1}{m_{HL}} = 2K_2 + 3K_3 m_{HL} \quad (19)$$

$$\frac{\frac{m_{HL}^{app}}{m_{HL}} - 1}{m_{HL}} = K_2 + K_3 m_{HL} \quad (20)$$

The corresponding values of K_2 and K_3 are gathered in Table 7. These values have been used to calculate the average number of aggregation (\bar{n}) as a function of extractant concentration

(Figure 3). A good agreement has been found between calculated and experimental values of \bar{n} .

Aggregation diagrams of the extractants as a function of the total concentration of extractants diluted in n-heptane have been calculated by using K_2 and K_3 (Figure 4). No trimer was observed in the extraction solvent containing UPA and EHPA while dimers and trimers exist in BiDiBOPP and IPA diluted in n-heptane. The dimerization and trimerization constants are very low compared to those determined by Buch et al. for D2EHPA in n-heptane ($K_2 = 115, K_3 = 3286$) likely because of the high steric hindrance of the organophosphorus acids synthesized in the present work, which may not favor hydrogen bonds and may destabilize the aggregates [27].

3.3. Partition coefficient

The partition coefficients of the organophosphorus compounds (P) between 1 mol.L⁻¹ HCl and HL diluted in n-dodecane is defined by the following equation:

$$HL \rightleftharpoons \overline{HL} \quad P = \frac{[\overline{HL}]}{[HL]} \quad (21)$$

where $[\overline{HL}]$ and $[HL]$ are the concentrations of the monomeric form of the organophosphorus acid in the organic phase and in the aqueous phase, respectively.

$[HL]$ can be expressed as:

$$[HL] = \frac{S_{HL}}{\left(1 + \frac{K_a}{[H^+]}\right)} \quad (22)$$

where S_{HL} is the solubility of the organophosphorus acid in the aqueous phase determined by colorimetric titration.

$[\overline{HL}]$ can be calculated by solving the following equation:

$$[\overline{HL}]_0 = [\overline{HL}] + 2 [(\overline{HL})_2] + 3 [(\overline{HL})_3] = [\overline{HL}] + 2K_2 [(\overline{HL})]^2 + 3K_3 [(\overline{HL})]^3 \quad (23)$$

where $[\overline{HL}]_0$, K_2 and K_3 are the initial concentration of the organophosphorus acid in the organic phase, the dimerization constant and the trimerization constant, respectively.

Table 8 gathers the partition coefficients of the monomeric form of the organophosphorus compounds calculated by using Eqs. (22) and (23). The partition coefficients of the monomeric form of the synthesized extractants are between 10 and 100 times greater than

those obtained for commercial extractants. The hydrophobicity of the synthesized extractants is obviously higher since the length of the hydrocarbon chains are longer.

4. Conclusion

The chemical structure of the organophosphorus extractants influences the acidic properties and the aggregation behavior. The values of pK_a are strongly affected by the presence of oxygen atoms in the alkyls chains. It appears that pK_a values increase in the following order: phosphoric acid < phosphonic acid < phosphonic acid and the presence of sulphur increases the acidity of the molecules. Conversely, there is no significant influence of the hydrophobicity of the extractants on their acidity strength. Aggregation characterization shows that bis(undécane-6-yl) phosphoric acid (UPA) exhibits a weak association while the two isomers, bis(1,3-dibutoxypropan-2-yl) phosphoric acid (BiDiBOPP) and bis(1,3-diisobutoxypropan-2-yl) phosphoric acid (IPA) form more dimers and trimers. All synthesized extractants exhibit very low aggregation constants compared to D2EHPA likely because of the high steric hindrance, which may not favor hydrogen bonds and may destabilize the aggregates.

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1. TABLE

TABLE 1: Organophosphorus compounds studied in the present work.

Acronym	Name	Structure
BiDiBOPP (4a)	bis(1,3-dibutoxypropan-2-yl) phosphoric acid	
IPA (4b)	bis(1,3-diisobutoxypropan-2-yl) phosphoric acid	
TPA (4c)	bis(5,8,12,15-tétraoxanonadécan-10-yl) phosphoric acid	
UPA (4d)	bis(undécan-6-yl) phosphoric acid	
EHPA (4e)	bis(1,3-di-2-éthylhexyloxypropan-2-yl) phosphoric acid	
Cyanex® 272	bis(2,4,4-triméthylpentyl) phosphinic acid	
Cyanex® 301	bis(2,4,4-triméthylpentyl) dithiophosphinic acid	
Ionquest® 801	2-éthylhexyl-2-éthylhexyl phosphonic acid	
D2EHPA	bis(2-éthylhexyl) phosphoric acid	

Table 2: Reaction yields for the synthesis of new extractants.

#	Name	Yield %
4a	bis(1,3-dibutoxypropan-2-yl) phosphoric acid (BiDiBOPP)	78
4b	bis(1,3-diisobutoxypropan-2-yl) phosphoric acid (IPA)	90
4c	bis(5,8,12,15-tetraoxanonadecan-10-yl) phosphoric acid (TPA)	84
4d	bis(undecan-6-yl)phosphoric acid (UPA)	92
4e	bis(1,3-di-2-ethylhexyloxypropan-2-yl) phosphoric acid (EHPA)	77

Table 3: Purities (%P) of the extractants synthesized in the present work determined by molecular Mass Spectroscopy (MS), Ionization Electrospray molecular Mass Spectroscopy (ESI-MS), ³¹P NMR, ¹³C NMR and ¹H NMR spectroscopy.

Extractants	MW (g.mol ⁻¹)	%P (MS)	%P (ESI-MS)	%P (³¹ P NMR)	%P (¹ H NMR)	%P (¹³ C NMR)	Estimated purity, %
IPA	470	99	99	97	94	99	94
UPA	406	99	99	94	92	99	92
TPA	646	99	99	98	93	99	93
BiDiBOPP	470	99	99	100	96	99	96
EHPA	695	99	99	93	92	99	92

Table 4: Impurities identified in UPA and EHPA.

Extractants	Chemical shift (ppm)	Impurity structure
UPA	-14	
EHPA	-13	

Table 5: Buffer solutions in water/ethanol mixtures for the determination of pK_a values by potentiometric titration [12, 13].

Ethanol, %(w/w)	pH (25 °C)	Buffer solutions	
		Compounds	Concentration, mol.kg ⁻¹
40.0	4.973	KHPh	0.05
	7.597	KH ₂ PO ₄	0.025
		Na ₂ HPO ₄	0.025
	5.395	HOAc	0.05
		NaOAc	0.05
52.0	2.79	NaCl	0.008840
		HCl	0.002210
	5.40	NaCl	0.00553
		HOAc	0.0221
	6.92	TEA	0.00221
		TEA-HCl	0.00442
73.4	2.88	NaCl	0.009352
		HCl	0.002338
		NaCl	0.00585
	6.06	HOAc	0.0234
		NaOAc	0.0117
	6.75	TEA	0.00234
		TEA-HCl	0.00468
85.4	3.01	NaCl	0.009688
		HCl	0.002422
		NaCl	0.00605
	6.65	HOAc	0.0242
		NaOAc	0.0121
	6.74	TEA	0.00242
		TEA-HCl	0.00484

Table 6: Experimental pK_a values of organophosphorus acids in aqueous solution of 1 mol.L⁻¹ KCl. ^a: pK_a values from [3, 25, 26], ^b: this work.

Extractants	pK_a (lit.) ^a	pK_a (exp.) ^b
Cyanex® 301	2,84	2.9
Cyanex® 272	3,73	4.2
Ionquest® 801	3,30	3.0
D2EHPA	2,75	2.6
Bidibopp IPA	-	2.4
IPA	-	2.5
TPA	-	2.3
UPA	-	3.5

Table 7: Values of $K_{\text{extractant}}$ in $\Omega.kg.g^{-1}$, average molecular weight \bar{M} in $g.mol^{-1}$, average aggregation number \bar{n} of the extractants, dimerization constant (K_2) and trimerization constant (K_3) deduced by VPO.

Extractant	$K_{\text{extractant}}$, $\Omega.kg.g^{-1}$	\bar{M} , $g.mol^{-1}$	\bar{n}	K_2 , $L.mol^{-1}$	K_3 , $L^2.mol^{-2}$
Bidibopp	2.8147	699	1.50±0.23	3	9
IPA	2.9646	680	1.50±0.19	6	10
UPA	4.17	483	1.20±0.14	2	0
EHPA	2.3785	847	1.20±0.12	4	0

Tableau 8: Partition coefficients (P) of the monomeric form of organophosphorus acids (HL) between an organic phase containing 0,1 mol.L⁻¹ HL in n-dodecane and 1 mol.L⁻¹ HCl (temperature = 25 °C). Partition coefficients have been calculated by using Eq. 22 and constants reported in Tables 6 and 7.

HL	P
Cyanex272	657
Cyanex301	1231
Ionquest801	88
D₂EHPA	211
Bidibopp	40539
IPA	34873
TPA	30000
UPA	13252
EHPA	31723

FIGURES

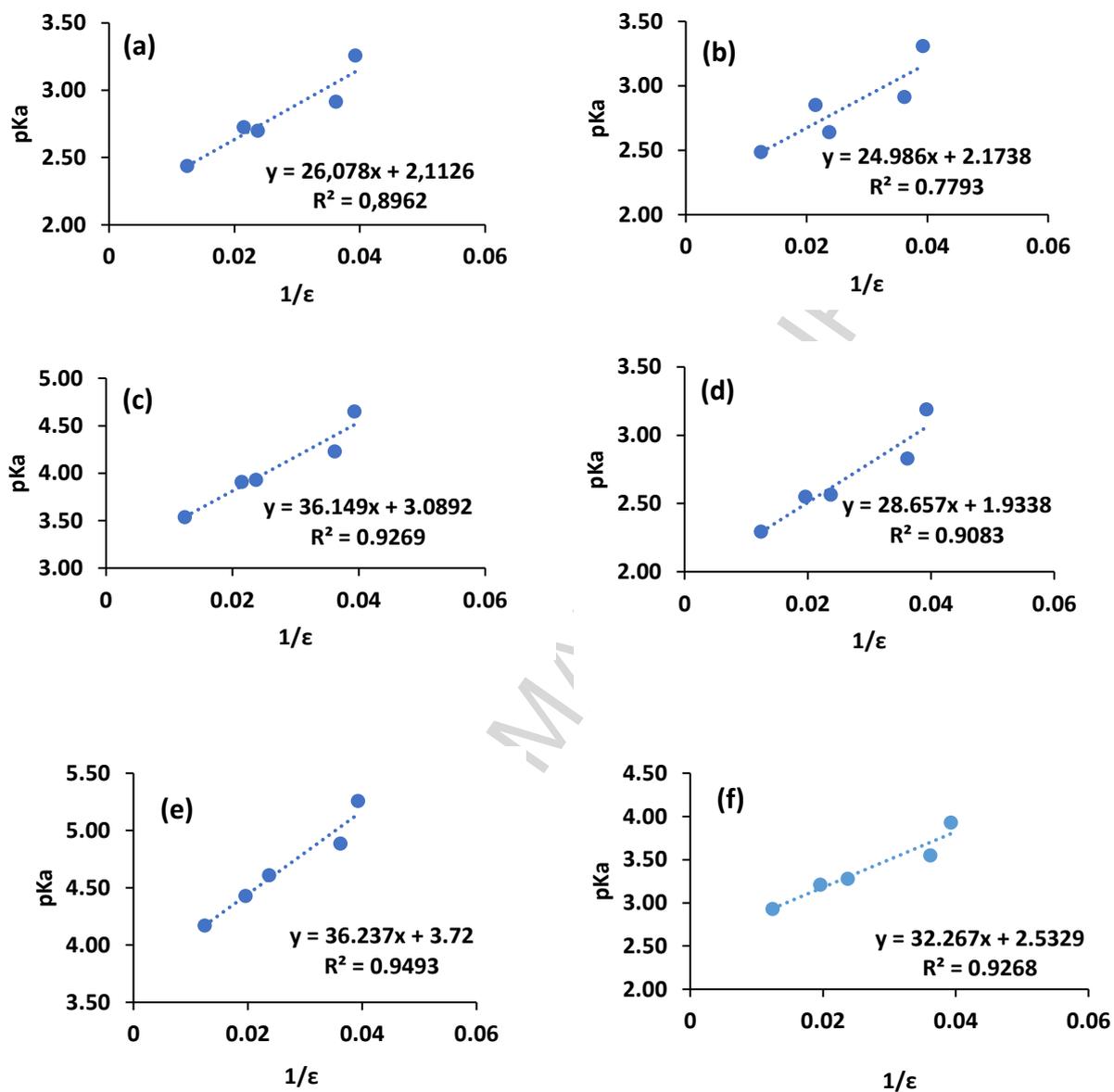


Figure 1: Variation of pK_a as a function of $1/\epsilon$ for (a) Bidibopp, (b) IPA, (c) UPA, (d) TPA, (e) Cyanex 272, (f) D2EHPA in water/2-propanol mixtures (temperature = 25 °C).

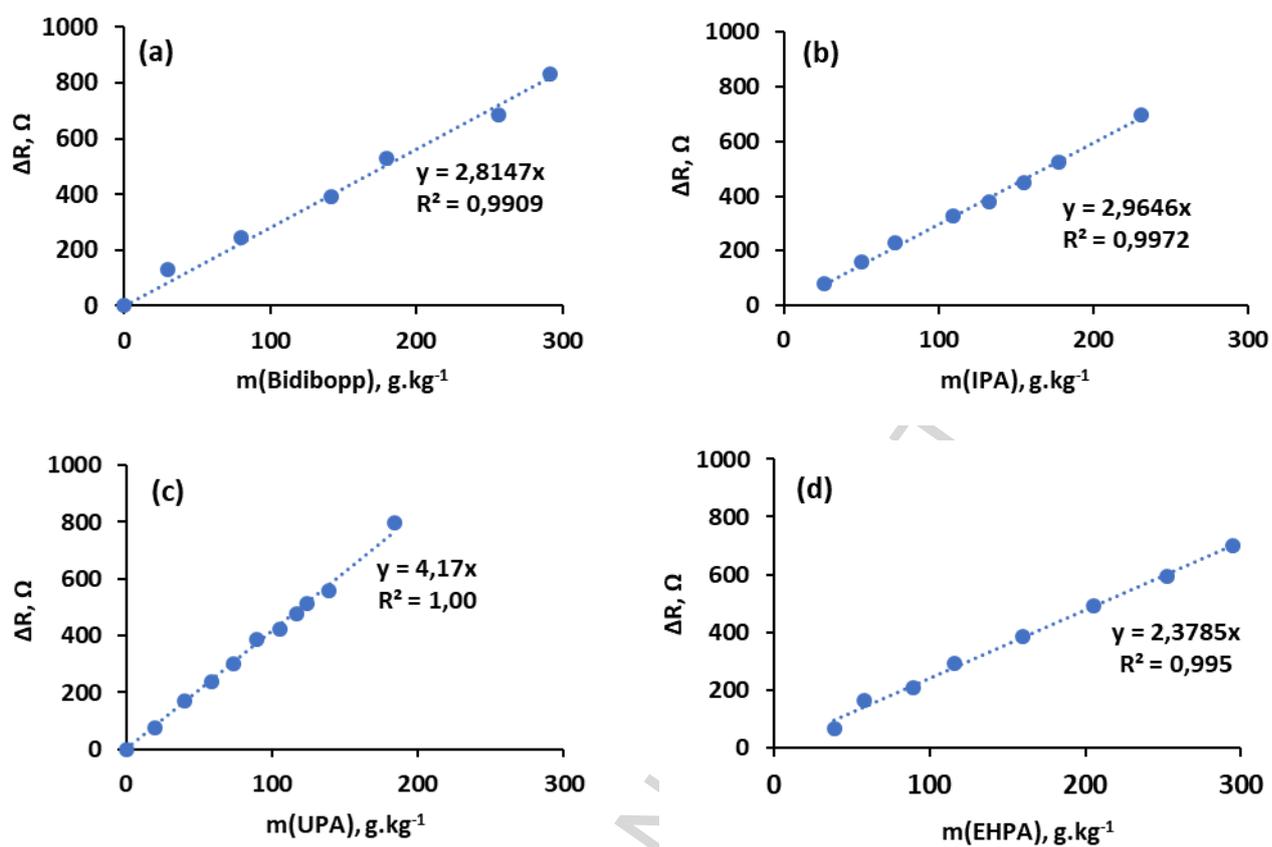


Figure 2: Difference in resistance between the thermistor (ΔR) measured during VPO experiments plotted as a function of the total solute concentration for (a) Bidibopp, (b) IPA, (c) UPA, (d) EHPA diluted in n-heptane (temperature=25 °C).

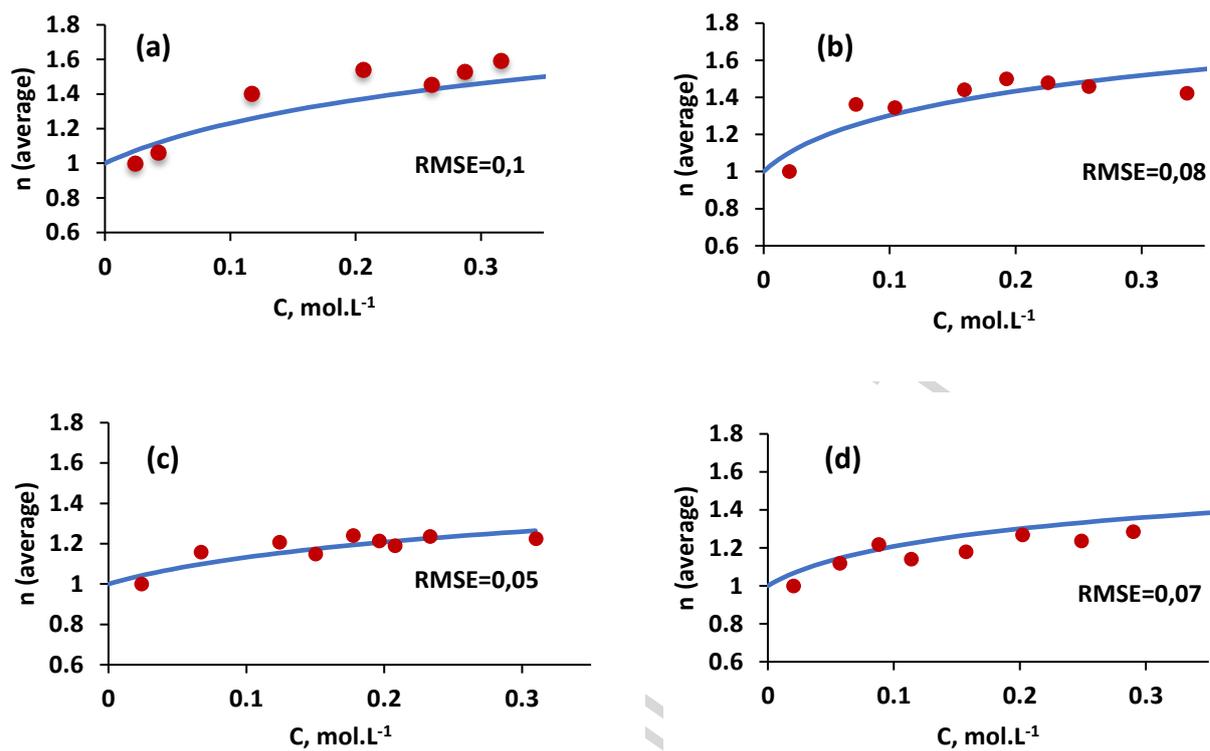


Figure 3: Aggregation number as a function of the total organophosphorus acid concentration for (a) Bidibopp, (b) IPA, (c) UPA, (d) EHPA diluted in n-heptane (temperature=25 °C). The full drawn lines were calculated by using the dimerisation and trimerisation constants reported in Table 7.

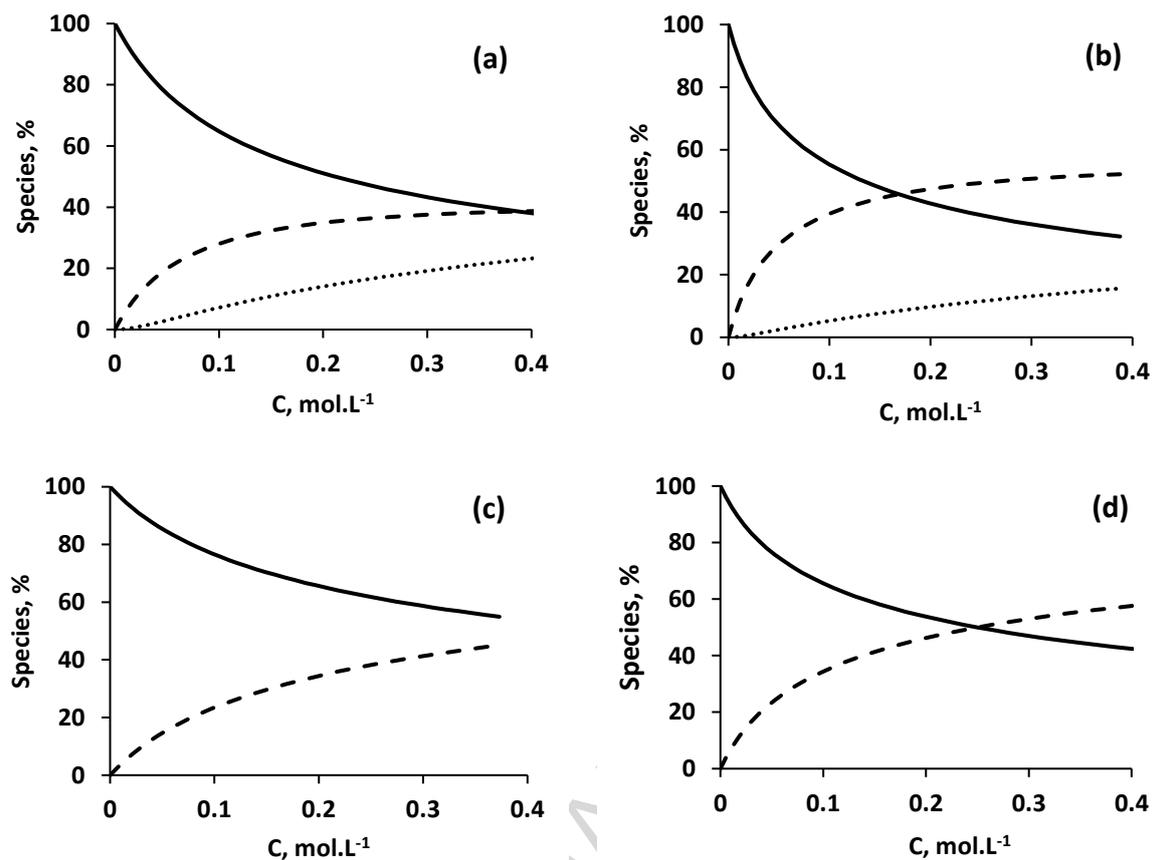


Figure 4: Aggregation distribution diagrams as a function of the total concentration of (a) Bidibopp, (b) IPA, (c) UPA, (d) EHPA diluted in n-heptane (—: monomer, ---: dimer,: trimer; temperature=25 °C).

Highlights

- Acidic properties and aggregation behaviour of extractants have been determined by potentiometry and VPO measurements.
- Steric hindrance destabilizes the aggregates
- The presence of oxygen atoms in the alkyl chains of the extractants is responsible for a decrease of the pKa values.

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