

Extraction of iron(III) from acidic sulfate solutions with bis(2-ethylhexyl)phosphoric acid in PENRECO[®] 170 ES, a new friendly diluent

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Abstract: The extraction of iron(III) from acidic sulfate solutions by bis(2-ethylhexyl)phosphoric acid (HDEHP) is investigated by using PENRECO[®] 170 ES as a diluent. PENRECO[®] 170 ES is new diluent which offers advantages such as improved solvency power, more complete phase disengagement and reduced losses in aqueous streams, with reductions of over 50% in diluent usage after 1 year, compared with conventional paraffinic diluents. The chemical analyses performed in the present work suggest that such properties arise, at least in part, from the presence of a series of hydrophobic branched alcohols in its composition (at least 0.6 mol dm⁻³). In spite of the solvation effects due to these alcohols, HDEHP is dimeric in this diluent and, in the presence of an excess of HDEHP, the extraction of iron(III) takes place according to the classical equation: $\text{Fe}^{3+} + 3\text{H}_2\text{L}_2 \rightleftharpoons \text{FeL}_3 \cdot 3\text{HL} + 3\text{H}^+$ with $K_{\text{ex}} = 10^{5.7 \pm 0.2}$ (at $I = 1 \text{ mol dm}^{-3}$). Such a value of K_{ex} is similar to that reported for pure hexane, which shows that the presence of long chain alcohols in PENRECO[®] 170 ES has no perceptible influence on the thermodynamics of iron(III) extraction by HDEHP. The extraction of iron(III) by HDEHP in PENRECO[®] 170 ES is slightly more rapid than in kerosene, which indicates that the molecules of alcohols constituting PENRECO[®] 170 ES have no negative effect on the kinetics of metal extraction although they compete with the extractant molecules for adsorption at the liquid–liquid interface. Stripping of iron(III) from loaded organic solutions by sulfuric acid is easy and rapid (95% equilibrium reached within 2 min) when HDEHP is used at moderate concentrations (typically 0.1 mol dm⁻³). At higher HDEHP concentrations, stripping is difficult and incomplete, as found previously with other diluents. Thus, PENRECO[®] 170 ES is interesting in its ability to overcome some of the physical problems encountered in liquid–liquid operations, but its use does not modify significantly the chemistry of iron(III) extraction by HDEHP.

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Keywords: solvent extraction; iron; bis(2-ethylhexyl)phosphoric acid; hydrophobic branched alcohols

1 INTRODUCTION

The removal of iron from industrial solutions is important in hydrometallurgy as iron is common in ores. Although the extraction of this metal by different extractants has been extensively investigated over several decades,^{1–10} all the proposed techniques still have some drawbacks, such as difficulties in extracting iron efficiently from highly acidic solutions, poor selectivity, problems in the stripping of iron from loaded organic phases, etc. In an attempt to overcome such difficulties, a series of oil-soluble aminomethylenephosphonic acid derivatives tailor-made for the selective extraction of iron(III) has been proposed.¹¹ In particular, (i-C₈H₁₇)₂NCH₂PO(OH)₂ and (oleyl)-[CH₂PO(OH)₂]₂N-(CH₂)₃-N[CH₂PO(OH)₂]₂ denoted hereafter EU2 and EU5/6, respectively, were

found to be more efficient than bis(2-ethylhexyl)phosphoric acid (HDEHP), considered here as a reference compound, as far as the extraction of iron(III) from acidic sulfate media is concerned. However, the stripping of iron(III) from loaded EU2 and EU5/6 organic phases is more difficult than from HDEHP solutions, which is a serious drawback although iron stripping can be achieved under certain reductive conditions.¹² On the other hand, when bis(2-ethylhexyl)phosphonic acid [PIA-8, Daihachi Chemical Industries, Japan] or bis(2,4,4-trimethylpentyl)phosphonic acid [Cyanex[®] 272, Cytec Industries, Inc, USA] are used as extractants, iron(III) can be much more readily stripped from the loaded organic phases (eg with 1.5 mol dm⁻³ H₂SO₄), but its extraction is not quite so strong when compared with HDEHP.^{2,13} As a

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result, HDEHP still appears as an appropriate compromise to extract iron(III) from highly acidic solutions.

In addition to the specific difficulties mentioned above, other general problems may be experienced during the liquid–liquid extraction of iron(III), such as poor phase disengagement and losses of organic solvent. Indeed, poor phase disengagement during solvent extraction is a problem frequently encountered in the mining industry where leach solutions often contain particulate matter and other undesirable material. In extreme cases these stable emulsions can result in the formation and/or accumulation of solid material, known as crud, at the interface. Furthermore, the coalescence of the smallest droplets of solvent formed during mixing is often incomplete and this results in losses of organic phase by entrainment in the raffinate. The factors affecting the separation of liquid–liquid dispersions have been discussed by various authors.^{14–18} In parallel to the fundamental studies cited above, an effort is currently being made to develop new diluents which facilitate phase disengagement and coalescence of the organic emulsions. Thus, a new diluent, commercially available as PENRECO[®] 170 ES (also known as CONOSOL[®] 170 ES) from Penreco, USA, has attracted our attention.¹⁹ Indeed, this diluent is claimed to exhibit improved solvency power and reduced overall losses in the aqueous streams compared with conventional paraffinic diluents. According to the technical brochure, several commercial operations that have switched to the exclusive use of PENRECO[®] 170 ES have had reductions of over 50% in diluent usage after 1 year.¹⁹

The aim of the present work was to understand the origin of the improved properties of PENRECO[®] 170 ES compared with conventional paraffinic diluents and to investigate possible modifications resulting from the use of this diluent on the extraction of iron(III) from acidic sulfate solutions. Indeed, it is well known that the nature of the diluent, as well as the presence of phase modifiers, may have a great influence on properties such as the self-association of extractants, the formation of third phases, adsorption at the interface, equilibrium distribution of metal species, the rate of extraction, etc.^{20–25} Bis(2-ethylhexyl)phosphoric acid was chosen here as a model extractant.

2 MATERIALS AND METHODS

2.1 Reagents

Bis(2-ethylhexyl)phosphoric acid having a purity of 96.5% (Albright & Wilson Americas), PENRECO[®] 170 ES diluent (Penreco¹⁹) and kerosene (Fluka) were used as delivered. All the other reagents of various origins were of analytical reagent grade.

2.2 Methods and apparatus

GC/MS analyses of PENRECO[®] 170 ES were per-

formed with a Shimadzu GCMS QP5050 A apparatus equipped with a SPB-5 column of 30m length and 0.25mm internal diameter. The oven temperature programme was as follows: 80°C (2min), 80°C to 250°C with an increase rate of 12°C min⁻¹, 250°C (10min). Mass spectra were obtained with a transfer line at 250°C and a mass window (*m/z*) ranging between 40 and 400 amu. The infrared spectra were recorded with a Perkin Elmer 1600 FTIR spectrometer. The extraction and stripping experiments were carried out at 25±1°C by shaking the mixture of aqueous and organic solutions inside a pear-shaped vessel whose movement was reproducible. Iron was determined in aqueous phases by colorimetry by using *o*-phenanthroline as an indicator, after reduction into iron(II).²⁶

3 RESULTS AND DISCUSSION

3.1 Composition and properties of PENRECO[®] 170 ES

The composition of PENRECO[®] 170 ES as determined by GC/MS and its main physical properties are given in Table 1. Examination of this table shows that PENRECO[®] 170 ES contains at least 15% (ie about 0.6mol dm⁻³) of various long chain alcohols. Such alcohols play the role of phase modifiers. Their presence may explain the improved solvency power of PENRECO[®] 170 ES and the ability of the latter to improve the phase separation compared with conventional paraffinic diluents.²⁰ In fact, the influence of alcohols on phase disengagement is complex and depends both on the composition of the system and, for a given system, on the nature of the continuous phase (aqueous or organic).^{14,27,28} In the experiments reported below, performed with synthetic solutions and in the absence of particulate matter, the time for 100% phase disengagement ranged between 30 and 60s, at 25°C. Because PENRECO[®] 170 ES is a complex mixture of hydrocarbons and alcohols having various degrees of branching and various lengths of alkyl chains, it could be expected that its composition might change during operation due to differential component loss to the aqueous phase. According to the available information, this problem does not seem to have been encountered in commercial operations,¹⁹ which is in good agreement with the fact that all the alcohols present in PENRECO[®] 170 ES are highly hydrophobic.

3.2 Predicted behaviour of HDEHP in PENRECO[®] 170 ES and at the aqueous/PENRECO[®] 170 ES interface

Bis(2-ethylhexyl)phosphoric acid is well known to be dimeric in diluents of low polarity.^{23,29,30} Trimeric species have also occasionally been reported.³¹ It is also well known that long chain alcohols often used as phase modifiers may solvate extractant molecules and, as a result, have the tendency to depress the self-association of the latter in organic phases. For

Component ^a	Retention time (min)	Molecular mass	% (from peak area)
<i>Alkanes</i>			
2,6-Dimethylundecane	9.71	184	2.0
2-Butyl-1,1,3-trimethylcyclohexane	9.94	182	1.5
2-Cyclohexyldodecane	10.15	252	1.5
2,7,10-Trimethyldodecane	10.66	212	3.6
2-Cyclohexyloctane	11.75	196	3.7
Eicosane	11.85	282	2.5
4-Methylpentadecane	11.92	226	3.2
Pentacosane	12.00	352	5.9
2,6,10,14-Tetramethylhexadecane	12.10	282	4.2
Octacosane	12.57	394	1.8
Nonacosane	13.87	282	2.9
<i>Alcohols^b</i>			
2-Propyl-1-heptanol	10.43	158	2.2
2-Hexyl-1-decanol	11.05	242	2.4
Tetradecanol	11.11	214	1.7
2-Butyl-1-octanol	11.25	186	3.5
2-Ethyl-1-decanol	11.81	186	2.8
Heptadecanol	13.22	256	2.1
<i>Unidentified hydrocarbons (including aromatics <5%)^c</i>			
Benzene <1 ppm			52.5
Toluene <1 ppm			
Physical properties		Specific gravity (15.5°C): 0.819 Flash point: 82°C Distillation: 199–274°C	

^a Identified by GC/MS.

^b The presence of —OH groups was confirmed by a strong and broad band in the 3600–3200 cm⁻¹ range in the IR spectrum.

^c PENRECO documentation.¹⁹

Table 1. Composition and physical properties of PENRECO[®] 170 ES

instance, bis(2-ethylhexyl)phosphoric acid is monomeric in *n*-decanol.³² The presence of a long chain alcohol may also slightly reduce the extraction of metal cations. Thus, addition of 10% isodecanol to 20% HDEHP in Shellsol[®] D70 (an aliphatic diluent from Shell) moves the pH_{0.5} value of Zn²⁺ from pH 1.15 to pH 1.45 (pH_{0.5}=pH at 50% extraction).³³ Although no quantitative data are available about the self-association of HDEHP in PENRECO[®] 170 ES, some predictions can be made from literature data, as reported in Table 2. In this table, the influence of isodecanol (a possible model of the long chain alcohols present in PENRECO[®] 170 ES) on the self-association

of HDEHP in *n*-decanol is considered. To perform the calculation, the three following assumptions were made:

- isodecanol (denoted ROH) forms tetrameric species in *n*-decanol with a formation constant of 50 (mol⁻³ dm⁹);^{34–36}
- the dimerization constant of HDEHP in *n*-decanol is equal to 3.2 × 10⁴ (mol⁻¹ dm³);²³
- isodecanol and HDEHP react to form the solvate HL.ROH characterized by a formation constant of 3 × 10² (mol⁻¹ dm³).²³

$[\overline{\text{HDEHP}}]_{\text{total}} \text{ (mol dm}^{-3}\text{)}$	$[\overline{\text{ROH}}]_{\text{total}} \text{ (mol dm}^{-3}\text{)}$			
	0	0.5	1	2
0.5	as H ₂ L ₂ :>99.5 as HL.ROH:0 as HL:<0.5	as H ₂ L ₂ :73 as HL.ROH:27 as HL:<1	as H ₂ L ₂ :65 as HL.ROH:34 as HL:<1	as H ₂ L ₂ :58 as HL.ROH:41 as HL:<1
0.1	as H ₂ L ₂ :99 as HL.ROH:0 as HL:<1	as H ₂ L ₂ :47 as ROH.HL:52 as HL:<1	as H ₂ L ₂ :39 as ROH.HL:61 as HL:<1	as H ₂ L ₂ :32 as ROH.HL:68 as HL:<1

Table 2. Estimated percentages (% mol) of the various forms of HDEHP (HL) in *n*-decanol in the presence of isodecanol (ROH)

Table 3. Estimated interfacial molar fractions of HDEHP (x_{HL}^{int}) and isodecanol (x_{ROH}^{int}) at the 0.1 mol dm⁻³ HCl/*n*-decane interface, as a function of isodecanol concentration²³

$[\overline{HDEHP}]_{total}$ (mol dm ⁻³)	$[\overline{ROH}]_{total}$ (mol dm ⁻³)			
	0	0.5	1	2
0.5	$x_{HL}^{int} = 1$ $x_{ROH}^{int} = 0$	$x_{HL}^{int} = 0.79$ $x_{ROH}^{int} = 0.21$	$x_{HL}^{int} = 0.73$ $x_{ROH}^{int} = 0.27$	$x_{HL}^{int} = 0.67$ $x_{ROH}^{int} = 0.33$
0.1	$x_{HL}^{int} = 1$ $x_{ROH}^{int} = 0$	$x_{HL}^{int} = 0.56$ $x_{ROH}^{int} = 0.44$	$x_{HL}^{int} = 0.47$ $x_{ROH}^{int} = 0.53$	$x_{HL}^{int} = 0.40$ $x_{ROH}^{int} = 0.60$

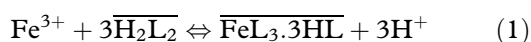
Table 2 indicates that HDEHP should exist in significant proportions both as the solvate HL.ROH and under its dimeric form H₂L₂ in the presence of isodecanol. A similar situation can be expected in PENRECO[®] 170 ES which contains at least 0.6 mol dm⁻³ of various long chain alcohols.

From another point of view, HDEHP molecules are surface active and adsorb at the aqueous/organic interfaces, which is an interesting feature for rapid metal extraction. However, in a previous work it was shown that the molecules of long chain alcohols such as isodecanol compete with HDEHP for adsorption at the liquid–liquid interfaces.²³ In fact, Table 3 shows that there is indeed competition, but that the HDEHP molecules remain present at the interface, even in the presence of isodecanol at high concentration. Logically, the same phenomenon should occur when PENRECO[®] 170 ES is used as a diluent and the presence of HDEHP at the interface should be not very strongly depressed.

The preceding considerations suggest that HDEHP should be less dimerized in PENRECO[®] 170 ES than in classical organic diluents, but with a preserved access to the liquid–liquid interface. However, such predictions are tentative because PENRECO[®] 170 ES is a complex mixture of hydrocarbons and alcohols having various degrees of branching and various lengths of alkyl chains, parameters which are known to have an influence on bulk and interfacial properties in liquid–liquid systems.^{23,37}

3.3 Thermodynamic aspects

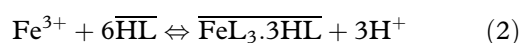
Various authors have reported that the extraction of iron(III) from acidic media by HDEHP in organic diluents such as benzene, hexane, etc takes place according to eqn (1):^{2,8–10}



with

$$K_{ex} = \frac{[\overline{FeL_3 \cdot 3HL}][H^+]^3}{[Fe^{3+}][\overline{H_2L_2}]^3}$$

where H₂L₂ represents the dimeric form of HDEHP and overbars refer to the organic species. Considering the above predictions on the self-association of HDEHP in PENRECO[®] 170 ES, eqn (2) should also be considered:



where HL denotes the solvate of HDEHP formed with the molecules of alcohol (eg HL.ROH). Depending on the relative contributions of eqn (1) and eqn (2) to the overall process of extraction, the logarithmic plot of the distribution coefficient of iron(III) versus the total concentration of free HDHEP ($C_{HDEHP, free}$) should lie between two straight lines whose slopes are equal to 3 (prevalence of eqn (1)) and 6 (prevalence of eqn (2)), respectively. Figure 1 shows that the plots log D_{Fe} vs log $C_{HDEHP, free}$ obtained at various acidities, in the presence of an excess of HDEHP compared with the quantity of iron to be extracted, are straight lines whose slopes are equal to 3 within the limits of uncertainty. This suggests that eqn (1) is prevalent in the process of iron(III) extraction by HDEHP in PENRECO[®] 170 ES and that HDEHP is mainly dimeric in the latter, in contrast to the predictions based on the properties of this extractant in *n*-decane

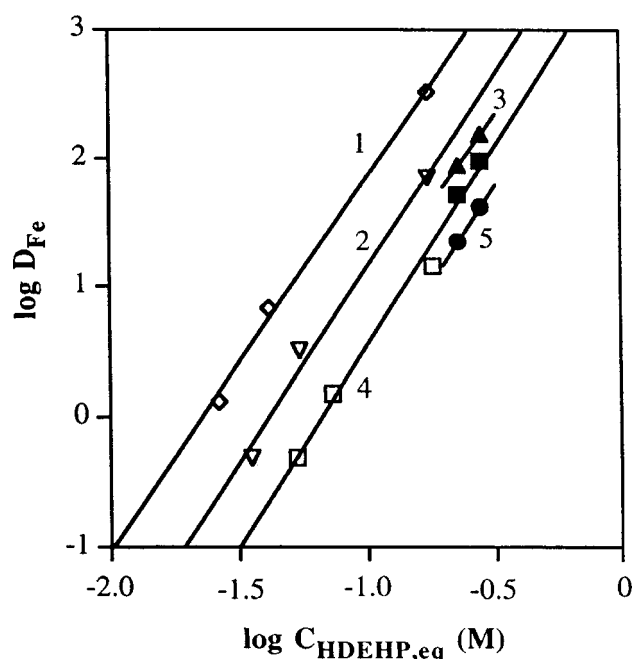


Figure 1. Logarithmic plot of D_{Fe} versus the total concentration of free HDEHP for the extraction of iron(III) from various aqueous phases (phase ratio = 1) ($C_{HDEHP, free} = [HL]_{free} + [HL]_{solvate, free} + 2[H_2L_2]_{free}$). Experimental conditions: (1) $[Fe(III)]_{initial} = 2.0 \times 10^{-2}$ mol dm⁻³ in 0.25 mol dm⁻³ H₂SO₄; (2) $[Fe(III)]_{initial} = 2.0 \times 10^{-2}$ mol dm⁻³ in 0.50 mol dm⁻³ H₂SO₄; (3) $[Fe(III)]_{initial} = 2.0 \times 10^{-3}$ mol dm⁻³ in 0.80 mol dm⁻³ H₂SO₄; (4) $[Fe(III)]_{initial} = 2.0 \times 10^{-3}$ mol dm⁻³ (full squares) or 2.0×10^{-2} mol dm⁻³ (open squares) in 1.0 mol dm⁻³ H₂SO₄; (5) $[Fe(III)]_{initial} = 2.0 \times 10^{-3}$ mol dm⁻³ in 1.25 mol dm⁻³ H₂SO₄; slopes of the straight lines: (1) 2.88, $r^2 = 0.996$; (2) 3.02, $r^2 = 0.988$; (3) 2.93, $r^2 = 1.00$; (4) 3.10, $r^2 = 0.989$; (5) 3.14, $r^2 = 1.00$.

Table 4. Values of $\log K_{ex}$ for extraction of iron(III) by HDEHP in PENRECO[®] 170 ES, benzene and hexane, at 25°C

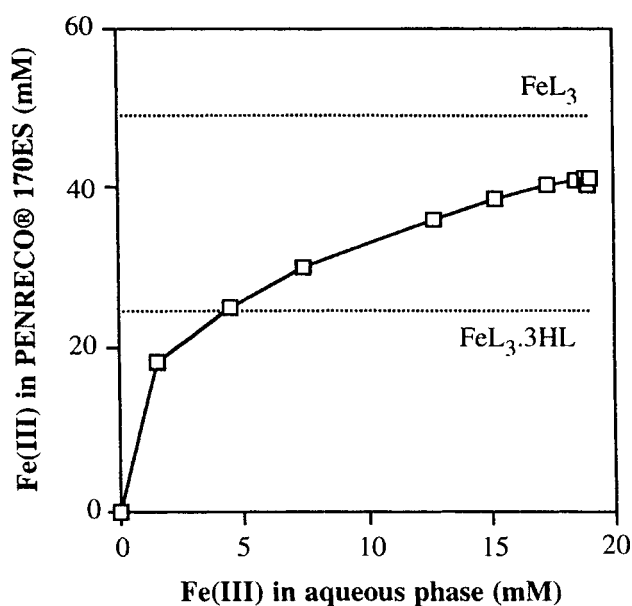
Diluent	Ionic strength	$\log K_{ex}$
PENRECO [®] 170 ES	$I = 1 \text{ mol dm}^{-3} (\text{H}_2\text{SO}_4)$	5.7 ± 0.2
Hexane ²	$I = 1 \text{ mol dm}^{-3} (\text{NaNO}_3)$	5.6
Benzene ⁸	$I = 1 \text{ mol dm}^{-3} (\text{NaClO}_4)$	3.1

modified by isodecanol. It should be noticed here that the slope of 3 obtained in the plot of $\log D_{Fe}$ vs $\log C_{HDEHP, free}$ in Fig 1 could also be interpreted by considering that the molecules of alcohols actively participate in the extraction process as assumed in eqn (3):



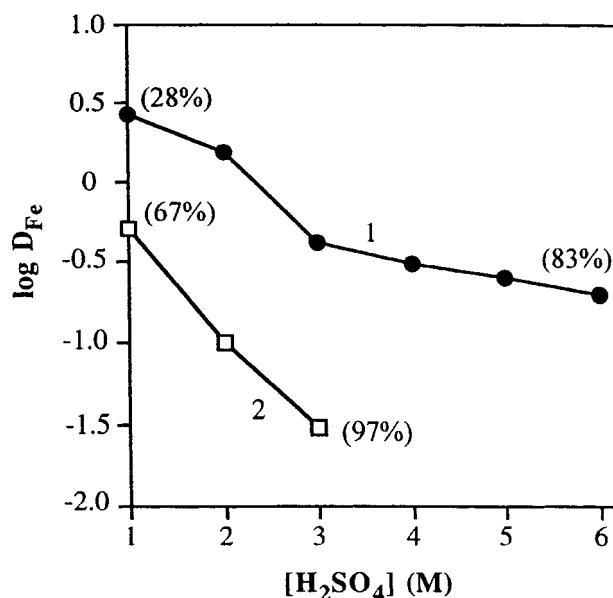
However, mixed complexes such as $\text{FeL}_3\cdot 3\text{ROH}$ have never been reported. Moreover, the extraction constant, K_{ex} , calculated for eqn (1) from the experimental data given in Fig 1 by taking into account the existence of iron(III) sulfate complexes^{38,39} is equal to $10^{5.7 \pm 0.2}$ (at $I = 1 \text{ mol dm}^{-3}$), which is similar to the value previously reported for the extraction of iron(III) by HDEHP in pure hexane (also at 25°C and $I = 1 \text{ mol dm}^{-3}$) (Table 4). This gives further evidence that eqn (1) is actually prevalent under the present experimental conditions and shows that the presence of long chain alcohols in PENRECO[®] 170 ES has no perceptible influence on the thermodynamics of iron(III) extraction by HDEHP. Table 4 also shows that the values of K_{ex} found both in hexane and PENRECO[®] 170 ES are much greater than that reported for benzene.

Figure 2 shows that eqn (1) applies only when the

**Figure 2.** Distribution isotherm of iron(III) between $0.1 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ and PENRECO[®] 170 ES containing $1.46 \times 10^{-1} \text{ mol dm}^{-3}$ HDEHP, at 25°C.

extraction of iron(III) takes place in the presence of a sufficient excess of HDEHP. Indeed, the asymptotic limit of the distribution isotherm obtained with an aqueous phase consisting of a $0.1 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ solution lies much beyond the boundary corresponding to the formation of $\text{FeL}_3\cdot 3\text{HL}$, which means that species exhibiting ligand/Fe molar ratios significantly lower than 6 also form at high loading. The formation of species such as FeL_3 can be assumed to explain this phenomenon as the formation of $\text{Fe}(\text{OH})\text{L}_2(\text{H}_2\text{L}_2)$ which is known to become prevalent above pH 2 can certainly be ignored at the selected acidity.⁴⁰ Finally, at high H_2SO_4 concentrations (ie $>4 \text{ mol dm}^{-3}$), iron(III) can also be extracted by HDEHP according to a solvation mechanism leading to the formation of $n\text{H}_2\text{Fe}_2(\text{SO}_4)_4\cdot m(\text{H}_2\text{L}_2)$ species.⁴⁰

Figure 3 shows that sulfuric acid can be used to strip iron(III) from the loaded organic solutions. It can be seen that the stripping is easier from lower concentrations of HDEHP. This phenomenon has already been reported for HDEHP in kerosene.⁴⁰ In fact, examination of the values of $\log D_{Fe}$ shows that the gap between curves 1 and 2 in Fig 3 cannot be interpreted only by the mass effect of HDEHP according to eqn (1), but that more complex phenomena take place. In particular, the observed difference may arise from the fact that the iron species initially present in the organic phases are not the same under the conditions of curve 1 $[(\overline{\text{HDEHP}}]_{\text{total}}/[\text{Fe(III)}])_{\text{initial}} \approx 7]$ and of curve 2 $[(\overline{\text{HDEHP}}]_{\text{total}}/[\text{Fe(III)}])_{\text{initial}} \approx 4]$. Finally, further examination of curve 1 shows that the effect of

**Figure 3.** Stripping of iron(III) from loaded HDEHP by sulfuric acid: $\log D_{Fe}$ versus sulfuric acid concentration in the aqueous stripping phase, at 25°C (phase ratio = 1) [the numbers in parenthesis indicate the percentage of stripping]. The loading of the HDEHP solutions was performed by extracting iron(III) from a $0.1 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ solution. Stripping conditions: (1) $[\text{Fe(III)}]_{\text{initial}} = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$, $[\overline{\text{HDEHP}}]_{\text{total}} = 1.46 \times 10^{-1} \text{ mol dm}^{-3}$; (2) $[\text{Fe(III)}]_{\text{initial}} = 2.4 \times 10^{-2} \text{ mol dm}^{-3}$, $[\overline{\text{HDEHP}}]_{\text{total}} = 9.64 \times 10^{-2} \text{ mol dm}^{-3}$.

H_2SO_4 concentration on the stripping of iron(III) is much weaker above 3 mol dm^{-3} than between 1 and 3 mol dm^{-3} . Such behaviour is a result of the tendency of iron(III) to remain in the organic phase by transformation of $\text{FeL}_3 \cdot 3\text{HL}$ into solvates such as $n\text{H}_2\text{Fe}_2(\text{SO}_4)_4 \cdot m(\text{H}_2\text{L}_2)$ at high H_2SO_4 concentration.⁴⁰ This phenomenon limits the efficiency of the stripping of iron(III) by H_2SO_4 and it is clear that use of PENRECO[®] 170 ES does not solve this difficulty.

3.4 Kinetic aspects

The extraction and stripping kinetics are investigated in Fig 4. This figure shows that the time needed to obtain the equilibrium at the extraction stage is about 8 min, whereas about 4 min are sufficient at the stripping stage, when PENRECO[®] 170 ES is used as the diluent. Figure 4 also shows that the extraction of iron(III) by HDEHP is slightly more rapid in PENRECO[®] 170 ES than in kerosene. This feature supports the fact that the molecules of HDEHP are not significantly excluded from the interface by the molecules of alcohols constituting PENRECO[®] 170 ES, the opposite of what was found with an oxyethylated octyl phenol having an average degree of oxyethylation of 5, whose addition significantly decreases the rate of iron(III) extraction by HDEHP.⁴¹ The slight increase of the rate of iron(III) extraction observed with PENRECO[®] 170 ES compared with kerosene could be as a result of a reinforcement of the hydrophilic nature of the interfacial zone, due to the presence of the hydroxyl groups of the adsorbed molecules of alcohols. Such a reinforcement may

favour the access of iron(III) species at the interface where the reaction with the HDEHP molecules takes place. The kinetics of stripping observed in Fig 4 are rather rapid, which is an interesting feature, even if the present conditions are favourable with a low concentration of HDEHP and high iron loading.

4 CONCLUSION

PENRECO[®] 170 ES offers advantages such as improved solvency power, more complete phase disengagement and reduced losses in aqueous streams, with reductions of over 50% in diluent usage after 1 year, compared with conventional paraffinic diluents.¹⁹ The analyses performed in the present work suggest that such properties arise, at least in part, from the presence of a series of hydrophobic alcohols in its composition (at least 0.6 mol dm^{-3}). It is also shown that the presence of such alcohols has no negative effect on the extraction of iron(III) by HDEHP. This can be explained by the fact that most of the alcohols present in PENRECO[®] 170 ES possess a bulky alkyl group in the neighbourhood of the hydroxyl function. Indeed, such branching has the tendency to inhibit both the association of these alcohols with HDEHP and their adsorption at the water/hydrocarbon interfaces, two phenomena which could have altered the thermodynamics and kinetics of iron(III) extraction.^{23,42,43}

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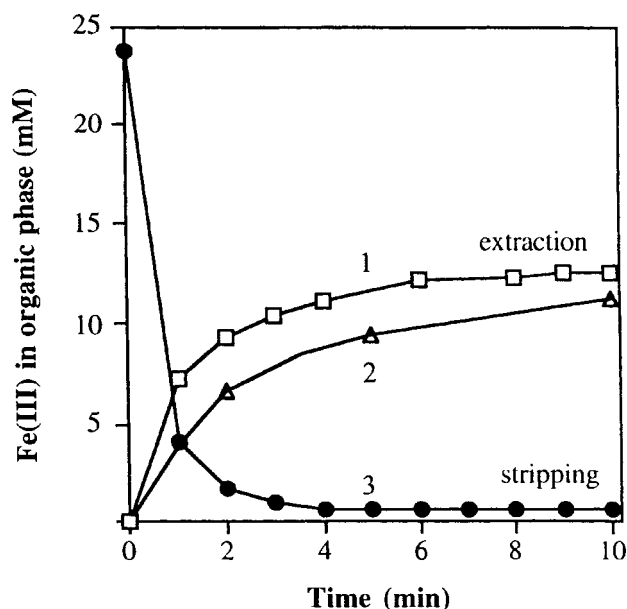


Figure 4. Kinetics of extraction and stripping of iron(III), at 25°C (phase ratio = 1). Extraction conditions: (1) diluent = PENRECO[®] 170 ES, $[\text{Fe(III)}]_{\text{initial}} = 1.6 \times 10^{-2} \text{ mol dm}^{-3}$ in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, $[\text{HDEHP}]_{\text{total}} = 9.64 \times 10^{-2} \text{ mol dm}^{-3}$; (2) diluent = kerosene, $[\text{Fe(III)}]_{\text{initial}} = 1.6 \times 10^{-2} \text{ mol dm}^{-3}$ in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, $[\text{HDEHP}]_{\text{total}} = 9.64 \times 10^{-2} \text{ mol dm}^{-3}$; stripping conditions: (3) diluent = PENRECO[®] 170 ES, $[\text{Fe(III)}]_{\text{initial}} = 2.4 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{HDEHP}]_{\text{total}} = 9.64 \times 10^{-2} \text{ mol dm}^{-3}$, stripping phase = $3 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$.

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