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Liquid–Liquid Extraction and Separation of a Macro Concentration of Fe^{3+}

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The liquid–liquid extraction of a concentrated (0.80 M) Fe^{3+} solution from the sulfuric acid medium has been proposed using a partially neutralized (15%) extractant solution of 30% (v/v) CYANEX 272 (= bis-(2,4,4-trimethylpentyl) phosphinic acid) + 30% (v/v) TBP (= tri-*n*-butyl phosphate) in ESCAID 110. The addition of TBP is required to achieve a clean phase separation. Speciation studies reveal that the presence of Fe^{3+} and $\text{Fe}(\text{SO}_4)_2^-$ as predominant aqueous phase species at an equilibrium pH of 1.2, Fe^{3+} reacts with the sodium form (NaR) of the extractant to form an extractable FeR_3 complex. The thermodynamic extraction constant of this reaction is found to be 1.8×10^{-2} . The kinetics of the extraction is slow at ambient temperature, but a reasonable rate of the mass transfer is achieved beyond 323 K, with the heat of the reaction being 159 kJ mol⁻¹. The extractant solution (30% or 1.1 M CYANEX 272) can load the metal ion up to a maximum of 34% of the reagent's initial molarity. Six stages of the countercurrent extraction are required to recover more than 99% of the 0.80 M Fe^{3+} . The stripping of the extracted Fe^{3+} has been carried out with a 2 M solution of sulfuric acid. The proposed conditions for the recovery of Fe^{3+} offer good selectivity with respect to metal ions, namely, Cr^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} . Using the optimized conditions, the leach liquor of a zinc concentrate has been purified from iron. Some advantages of the developed iron recovery process over the traditionally used jarosite precipitation method have been discussed.

Introduction

Iron contamination of leach solutions is one of the major problems in the hydrometallurgy of different base metals, including zinc, cobalt, nickel, etc. In most of the cases, the desired removal of iron is achieved by precipitating this impurity as a solid jarosite or goethite product.^{1–3} However, the disposal of the generated solid waste is seen as an environmental problem, mainly due to the presence of high contents of iron and other heavy metals in it. These metals may gradually leach under the ambient conditions to contaminate the soil and the groundwater. Furthermore, dumping of the solid waste in landfills takes up large surface areas and incurring costs related to the land and the treatment of leachates. For the last few decades, considerable efforts are being put to explore more environmentally friendly iron separation technologies. The use of liquid–liquid extraction has been seen as one of the most promising alternatives.⁴ Several classes of extractants, such as versatic acids,⁵ amines,^{6,7} and organophosphorus extractants,^{8–17} have been used to extract Fe^{3+} from the aqueous solutions. Even so, most of the proposed extractants do not satisfy technical requirements. Versatic acid is unsuitable for use in a highly acidic aqueous medium. DEHPA forms strong organic phase complexes with Fe^{3+} , but the stripping is not convenient and requires the use of concentrated HCl.⁹ Some alternative stripping routes have been suggested for the removal of Fe^{3+} from the loaded DEHPA phase. Reduction of iron³⁺ to iron²⁺ in the organic phase has been suggested as one of the options.^{10,11} This has been achieved at conditions of high temperature and pressure by reduction with zinc powder and H_2/SO_2 . Galvanic stripping has been attempted by several researchers.^{12–14} However, the process is not continuous. Some reports suggest the mixing of DEHPA^{3,15,16} with tri-*n*-butyl phosphate (TBP), tri-*n*-octyl phosphine oxide (TOPO), CYANEX 923, and amines to enable the use of sulfuric acid as a stripping reagent. Some recent

studies by Principe and Demopoulos¹⁷ have proposed the use of octylphenyl acid phosphate (OPAP) as an Fe^{3+} extractant. OPAP is claimed to provide better kinetics of iron extraction and offers greater pH functionality than DEHPA. Stripping of the loaded iron from both the extractants is achieved with 6 N HCl.

The industrial utility of any iron solvent extraction process is generally measured by the feasibility of the extractant regeneration. So far, only some coupled stripping–pyrohydrolysis processes have been suggested as technically viable. Apparently, more research is required in this area. Our earlier work¹⁸ on the separation of Fe^{3+} from a tannery filtrate indicated that CYANEX 272 can be an efficient Fe^{3+} extractant with the possibility of its easy regeneration using dilute sulfuric acid. Another available report¹⁹ also indicates the utility of CYANEX 272 for the removal of iron from cobalt liquors. Both of the quoted studies, however, dealt only with a dilute solution of iron (up to 0.5 g L⁻¹). Most of the industrial leach liquors may invariably encounter a much higher concentration of iron. The present study focuses the use of CYANEX 272 for the extraction of a macro concentration of Fe^{3+} from the sulfuric acid medium. Some important variables, influencing the extent and the rate of the mass transfer, have been investigated. The mechanism of the extraction process has been described, and the important physical parameters have been determined. An assessment has been made on the selectivity of the developed Fe^{3+} extraction system with respect to commonly associated metals, such as Cr^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} . The practical utility of the developed process has been demonstrated by attempting the separation of iron from the leaching solution of a zinc concentrate.

Materials and Procedure

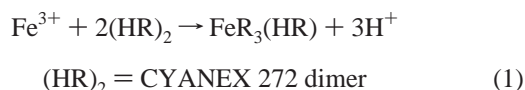
CYANEX 272 (85% purity), TBP (99% purity), and ESCAID 110 (200–248 °C fraction hydrocarbon fluid with 99.5% aliphatic content) were received from Cytec Netherlands, Merck UK, and ExxonMobil Spain, respectively. The working solutions

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of the extractant were prepared in the diluent, ESCAID 110. Their concentrations were determined by taking the initial purity of CYANEX 272 into account. All other chemicals were of analytical reagent grade from Merck UK. The working solutions of the metal ions were prepared by dissolving their suitable salts in the dilute sulfuric acid and making up the required volume with the deionized water. The pH values were measured with a Metrohm 827 pH lab pH meter using a Metrohm 6.0228.010 glass electrode.

The extractant solution was purified from the unwanted acidic impurities by washing it with an equal volume of 5% (w/v) Na_2CO_3 , followed by water. Some initial equilibration tests with the aqueous phase, containing 0.80 M Fe^{3+} (pH = 1.2), and the organic phase, containing 30% CYANEX 272 (supplied/purified reagent) in ESCAID 110 (v/v), figured out the problem of crud formation. Various modifiers, such as isodecanol, octanol, CYANEX 923, and TBP, were employed to improve the phase separation characteristics. Only TBP was found to produce satisfactory phase separations. All further investigations were carried out by using a 1:1 (v/v) mixture of CYANEX 272 (reagent without purification) + TBP as the extractant solution.

During the cation exchange extraction reaction of Fe^{3+} with CYANEX 272, the presence of labile H atoms in the extractant led to a proportional release of H^+ ions in the aqueous phase (eq 1).



The resulting reduction in the aqueous phase pH shifted the equilibrium to the left, thus stopping the mass transfer. This problem has been circumvented by partially neutralizing the extractant solution. Under the present experimental conditions ($\text{Fe}^{3+}_{\text{initial}} = 0.80$ M, initial pH = 1.2), 15% neutralization (in molar terms) of the extractant provided minimum variation in the aqueous phase pH during the extraction step. A required aliquot of the extractant solution was contacted with a calculated volume of 5 M NaOH. Equation 2, depicting the neutralization reaction, indicates that 1 mol of NaOH will completely neutralize $1/2$ mol of the dimer extractant. The volume of 5 M NaOH solution required to partially (15%) neutralize the taken volume of the extractant solution was calculated accordingly.



For the solvent extraction experiments, the aqueous and the organic phases, contained in 250 mL separating funnels (A/O = 1, unless reported), were contacted (150 rpm) in an orbital shaker (Aralab Agitorb 160 E) at a constant temperature. Wherever necessary, the pH of the aqueous phase was adjusted by adding suitable volumes of NaOH or H_2SO_4 solutions. After the separation of the equilibrated phases, the metal concentration in the aqueous phase was determined by atomic absorption spectroscopy (AAS) (instrument make AAnalyst 200, Perkin-Elmer). The metal concentration in the organic phase was computed by mass balance considering no change in the volumes of aqueous and organic phases during the equilibration. The stripping of the loaded organic phase was carried out at 323 ± 1 K by using 2 M H_2SO_4 (A/O = 1) as the reagent.

A representative leaching solution, loaded with a high concentration of iron, was produced by the oxidative leaching of a zinc concentrate (Somincor, Portugal) with 0.40 M $\text{Fe}_2(\text{SO}_4)_3$ and 0.50 M H_2SO_4 (S/L ratio = 10 g per 200 mL), in a five-necked round-bottom reactor (1 L, 13 cm in diameter) fitted

with an agitating (325 rpm) single round paddle impeller. The reaction temperature was maintained at 353 ± 3 K. Under the quoted conditions, the dissolution of zinc took place according to the following equation (eq 3)

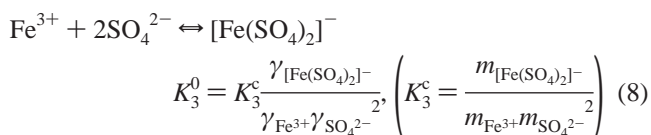
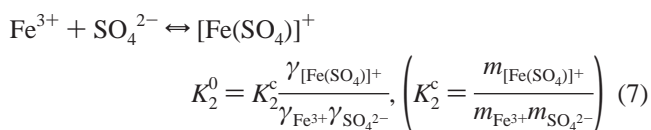
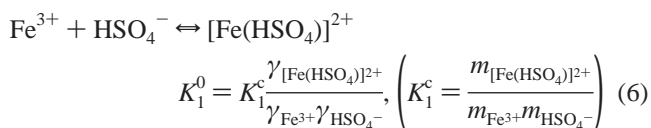
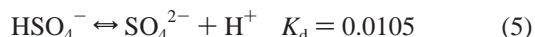
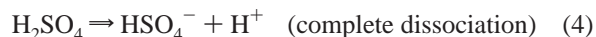


The above methodology ensured more than 95% recovery of zinc. The final total concentration of iron was 0.91 M; Fe^{+3} and Fe^{+2} being in a ratio of 20 and 80%, respectively. For the solvent extraction recovery of iron, the above obtained leaching solution (200 mL, initial pH = 0.25, $T = 298$ K), containing both the trivalent and bivalent forms of the metal ion, was oxidized by the reaction with 20 mL of 11.3 M H_2O_2 . The resulting solution was bubbled and gently heated. After allowing it to cool, the pH was adjusted to 1.2 by the addition of a NaOH/ H_2SO_4 solution. The final composition of the leaching solution, with respect to the major contents, was as follows: 13.6 g L^{-1} Zn, 43.1 g L^{-1} Fe, and 0.31 g L^{-1} Cu, pH = 1.2.

Results and Discussion

1. Modeling of the Fe^{+3} Species in the Aqueous Phase.

The present work deals with the extraction of 0.80 M Fe^{+3} in a medium of sulfuric acid (pH = 1.2). The aqueous phase used is a 0.40 M solution of $\text{Fe}_2(\text{SO}_4)_3$ in 0.50 M H_2SO_4 , treated with 0.91 M NaOH. Speciation of the different species in this aqueous phase is required to propose the mechanism of Fe^{3+} mass transfer in the extractant solution. The following equilibria can be expected to occur in the test solution



where " K_i^0 " and " K_i^c " ($i = 1, 2, 3$) denote the thermodynamic and apparent equilibrium constants, respectively, and " m_i " and " γ_i " are the molality and the activity coefficient, respectively. The formations of hydroxocomplexes, like $[\text{Fe}(\text{OH})]^{2+}$, $[\text{Fe}(\text{OH})_2]^+$, and $[\text{Fe}_2(\text{OH})_2]^{4+}$, need not to be considered at the applied experimental conditions.

The ratio of individual aqueous phase ferric species can be assessed by the linear regression of eqs 6–8 (portion in parentheses), along with the equations of mass balance (eqs 9–11) and charge balance (eq 12)

$$m_{\text{Fe}(\text{Total})} = m_{\text{Fe}^{3+}} + m_{[\text{Fe}(\text{HSO}_4)]^{2+}} + m_{[\text{Fe}(\text{SO}_4)]^+} + m_{[\text{Fe}(\text{SO}_4)_2]^-} \quad (9)$$

$$m_{\text{HSO}_4^-(\text{Total})} = m_{\text{HSO}_4^-} + m_{[\text{Fe}(\text{HSO}_4)]^{2+}} \quad (10)$$

$$m_{\text{SO}_4^{2-}(\text{Total})} = m_{\text{SO}_4^{2-}} + m_{[\text{Fe}(\text{SO}_4)]^+} + m_{[\text{Fe}(\text{SO}_4)_2]^-} \quad (11)$$

$$m_{\text{H}^+} + m_{\text{Na}^+} + 3m_{\text{Fe}^{3+}} + 2m_{[\text{Fe}(\text{HSO}_4)]^{2+}} + m_{[\text{Fe}(\text{SO}_4)]^+} = m_{\text{HSO}_4^-} + 2m_{\text{SO}_4^{2-}} + m_{[\text{Fe}(\text{SO}_4)_2]^-} \quad (12)$$

Estimations of K_i^c values are required to work out the above equations. These important values have to be computed with the help of K_i^0 and γ_i . The data on the K_i^0 values of the ferric ion–sulfuric acid interactions can be taken from the literature.^{20,21} The activity coefficients γ_i of encountered species needs to be determined. The Pitzer model (for H^+ , Na^+ , Fe^{3+} , HSO_4^- , and SO_4^{2-}) and the Debye–Hückel equation (for $[\text{Fe}(\text{HSO}_4)]^{2+}$, $[\text{Fe}(\text{SO}_4)]^+$, and $[\text{Fe}(\text{SO}_4)_2]^-$) have been used for the determination of individual γ_i . The main points of the adopted modeling techniques are summarized in the following text.

In a simple form, the Pitzer model describes the following equations for the cation “M” and the anion “X”

$$\ln \gamma_M = z_M^2 f' + 2 \sum_a m_a (B_{Ma} + EC_{Ma}) + z_M^2 \sum_c \sum_a m_c m_a B'_{ca} + z_M \sum_c \sum_a m_c m_a C_{ca} + \sum_c m_c (2\Theta_{Mc} + \sum_a m_a \psi_{Mca}) + \frac{1}{2} \sum_a \sum_d m_a m_d \psi_{Maa'} \quad (13)$$

$$\ln \gamma_X = z_X^2 f' + 2 \sum_c m_c (B_{cX} + EC_{cX}) + z_M^2 \sum_c \sum_a m_c m_a B'_{ca} + z_M \sum_c \sum_a m_c m_a C_{ca} + \sum_a m_a (2\Theta_{Xa} + \sum_c m_c \psi_{Xca}) + \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} \psi_{Xcc'} \quad (14)$$

In the above equations, the indexes “c” and “a” (having charge “ z_i ”) stand for other cations and the anions present in the solution with their molality to be “ m_i ”. The equivalent molality “ E ” is defined as $1/2 \sum m_i z_i$, and “ f' ” is the Debye–Hückel limiting law slope

$$f' = -A_\phi \left[\frac{I^{1/2}}{(1 + bI^{1/2})} + \frac{2}{b} \ln(1 + bI^{1/2}) \right] \quad (15)$$

At 298 K, “ A_ϕ ” has a value of $0.3914 (\text{mol kg}^{-1})^{1/2}$. Since the Pitzer equation does not explicitly account the differences in the effective size of the ions (\tilde{a}) present in a solution, the factor “ b ” (a product of “ β ” and “ \tilde{a} ”, where $\beta = 0.3288 (\text{mol kg}^{-1})^{1/2}$ and $\tilde{a} = 3.65 \text{ \AA}$) is given a generalized value of 1.2. The ionic strength “ I ” is expressed as $I = 1/2 \sum m_i z_i^2$.

In the Pitzer equation, the parameters “ Θ_{ij} ” and “ ψ_{ijk} ” respectively represent the binary interaction of similarly charged ions and the ternary interaction of two similarly charged ions with an ion of opposite charge. The values of Θ_{ij} and ψ_{ijk} are either negligible or so small that their omission in practical calculations is acceptable in most of the cases.²² The terms “ B_{Ma} ”, “ B'_{Ma} ”, “ B_{cX} ”, and “ B'_{cX} ” represent the short-range binary interactions of involved ions, and their values are computed with the help of two solute specific parameters, i.e., “ β_{ij}^0 ” and “ β_{ij}^1 ”.²² In the present study, the required values of the β_{ij}^0 and β_{ij}^1 terms for the interactions, namely H– SO_4 , H– HSO_4 , Na– SO_4 , Na– HSO_4 , Fe– SO_4 , and Fe– HSO_4 , have been taken, or approximated, from some earlier published

Table 1. Speciation–Modeling Conditions, Pitzer Parameters, and Results

Modeling Conditions				
molality ^a of different ions (mol kg^{-1})				
$m_{\text{Fe}^{3+}} = 0.81$, $m_{\text{H}^+} = 6.0 \times 10^{-2}$, $m_{\text{Na}^+} = 0.90$, $m_{\text{SO}_4^{2-}} = 1.33$, $m_{\text{HSO}_4^-} = 2.7 \times 10^{-2}$, pH = 1.2, $I = 6.80$				
Parameters				
	$\beta^0 (\text{kg mol}^{-1})$	$\beta^1 (\text{kg mol}^{-1})$	C^Φ	ref
H^+ , HSO_4^-	0.296	0.400	−0.006	20
H^+ , SO_4^{2-}	−0.008	0.315	−0.010	20
Na^+ , HSO_4^-	0.067	0.383	−0.004	20
Na^+ , SO_4^{2-}	0.020	1.113	0.005	20
Fe^{3+} , HSO_4^-	2.850	0	−0.355	19, 21
Fe^{3+} , SO_4^{2-}	0.566	12.2	0.001	19, 21

calculated γ	calculated K_i^c
$\gamma_{\text{H}^+} = 0.276$	$K_{[\text{Fe}(\text{HSO}_4)]^{2+}}^c = 85.5$
$\gamma_{\text{Na}^+} = 0.356$	$K_{[\text{Fe}(\text{SO}_4)]^+}^c = 0.387$
$\gamma_{\text{HSO}_4^-} = 20.4$	$K_{[\text{Fe}(\text{SO}_4)_2]^-}^c = 3.02$
$\gamma_{\text{SO}_4^{2-}} = 6.44 \times 10^{-2}$	
$\gamma_{\text{Fe}^{3+}} = 4.00 \times 10^{-4}$	
$\gamma_{[\text{Fe}(\text{HSO}_4)]^{2+}} = 0.210$	
$\gamma_{[\text{Fe}(\text{SO}_4)]^+} = 0.677$	
$\gamma_{[\text{Fe}(\text{SO}_4)_2]^-} = 0.677$	

Percentage Fractions of Fe^{3+} Species

$[\text{Fe}^{3+}] = 44.5\%$, $[\text{Fe}(\text{HSO}_4)]^{2+} = 3.2\%$, $[\text{Fe}(\text{SO}_4)]^+ = 9.8\%$,
 $[\text{Fe}(\text{SO}_4)_2]^- = 42.5\%$

^a Molality m_i = (molarity, M)/[(electrolyte density, g L^{-1}) − (0.001MW, $\text{g mol}^{-1} \times \text{molarity, M})]$.

data.^{21–23} The terms “ C_{Ma} ” and “ C_{cX} ” in eqs 13 and 14 were solved with the help of a solute specific numerical constant “ C_{ij}^Φ ”,²² whose values were also taken from the available data.^{21–23}

The activity coefficients of the ferric ion pairs have been estimated by using the Debye–Hückel equation (eq 16).

$$\log \gamma_{\pm} = \frac{-A_\gamma |z_M z_X| I^{1/2}}{1 + \beta \tilde{a}^{1/2}} \quad (16)$$

where “ A_γ ” and β are the constants with their respective values (at 298 K) of 0.509 and $0.3288 (\text{mol kg}^{-1})^{1/2}$. The term \tilde{a} refers to the effective size (in angstroms) of the ions. Generally, the Debye–Hückel estimations are recommended in relatively dilute solutions, e.g., up to 0.1 mol kg^{-1} . However, in several instances, this equation has also been successfully applied in concentrated solutions.^{20,24–26} Dry and Bryson²⁰ have justified the use of Debye–Hückel activity coefficients to predict the concentration of some iron sulfate complex species up to the ionic strength of about 4. They observed the calculated activity coefficients of $[\text{Fe}(\text{SO}_4)]^+$ and $[\text{Fe}(\text{SO}_4)_2]^-$ to be similar to those reported in the literature. More recently, Rosinda et al.²⁶ have reported the use of Debye–Hückel theory to determine the activity coefficients of copper species, e.g. $[\text{Cu}(\text{NH}_3)_4]^{2+}$, at an ionic strength of 3.24.

Table 1 lists the different parameters used to model the required activity coefficients. The sets of speciation equations were solved by the iterative “Solver” add-in of Microsoft Excel 2003. The results (Table 1) show that Fe^{3+} and $[\text{Fe}(\text{SO}_4)_2]^-$ are the predominant ferric species in the aqueous phase under the present experimental conditions. The Fe^{3+} forms an extractable complex with the extractant solution (30% CYANEX 272 + 30% TBP), thereby affecting the mass transfer.

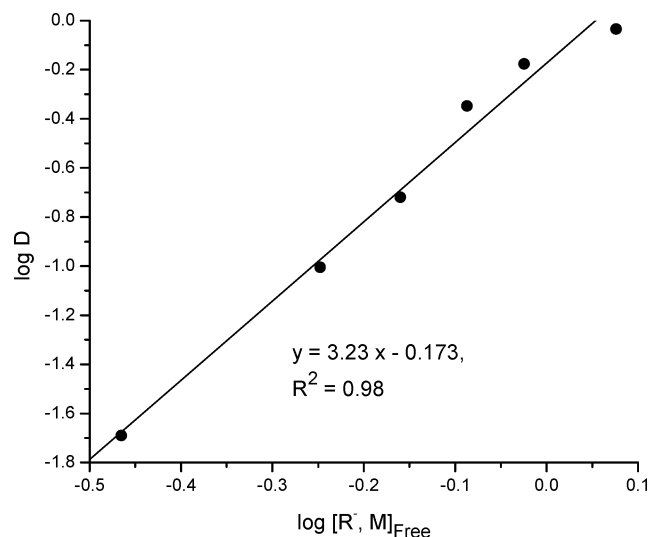


Figure 1. Extraction of Fe^{3+} as a function of free extractant $[\text{R}^-]$ concentration. Conditions: $[\text{Fe}^{3+}]_{\text{aqueous}} = 0.80 \text{ M}$, $[\text{CYANEX 272} + \text{TBP}]_{\text{organic}} = 10\% + 10\%$, $15\% + 15\%$, $20\% + 20\%$, $25\% + 25\%$, $30\% + 30\%$ (v/v in ESCAID 110, initially neutralized to 15% with respect to CYANEX 272), equilibrium pH = 1.2, $T = 298 \text{ K}$, $\text{A/O} = 1$, $t = 50 \text{ min}$.

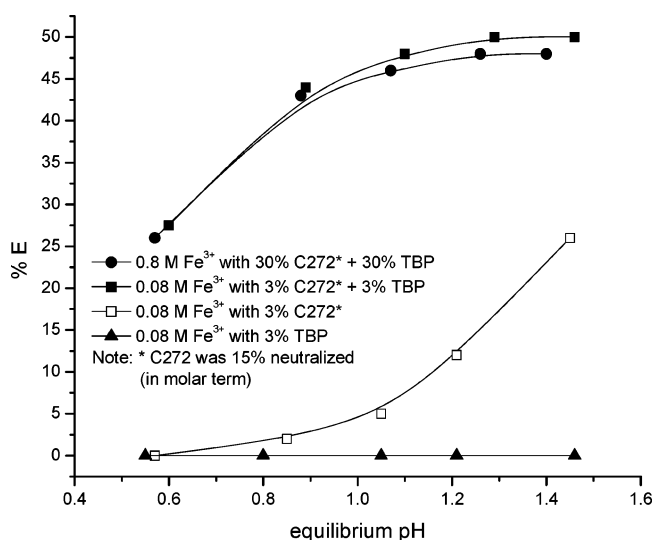


Figure 2. Extraction of Fe^{3+} with Cyanex 272, TBP, and Cyanex 272 + TBP mixture as a function of equilibrium pH. Conditions: $T = 298 \text{ K}$, $\text{A/O} = 1$, $t = 50 \text{ min}$.

2. Fe^{3+} Extraction as a Function of Extractant Composition and Equilibrium pH. The extraction of Fe^{3+} , at an equilibrium pH of 1.2, has been investigated with extractant solutions of varying compositions (5% CYANEX 272 + 5% TBP, 10% CYANEX 272 + 10% TBP, 15% CYANEX 272 + 15% TBP, 20% CYANEX 272 + 20% TBP, 25% CYANEX 272 + 25% TBP, 30% CYANEX 272 + 30% TBP). All these extractant solutions, with respect to CYANEX 272, were neutralized to a degree of 15%. The results of the study, taking the free extractant concentration $[\text{R}^-]$ in terms of molarity ($[\text{R}^-]_{\text{Free}} = [\text{R}^-]_{\text{Initial}} (\text{determined considering extractant dimerization}) - [\text{R}^-]_{\text{Complexed}} (\text{determined by } \%E)$), are shown in Figure 1. The slope analysis has confirmed the involvement of three extractant molecules in the formation of the extracting species. Hence, the following mechanism of the extraction process can be proposed.

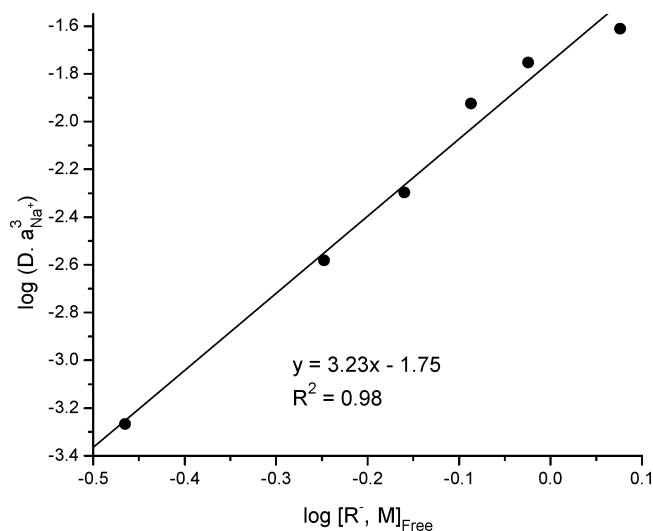
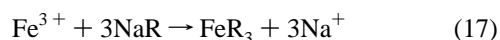


Figure 3. Determination of K_{ext}^0 . Conditions: $[\text{Fe}^{3+}]_{\text{aqueous}} = 0.80 \text{ M}$, equilibrium pH = 1.2, $T = 298 \text{ K}$, $\text{A/O} = 1$, $t = 50 \text{ min}$.

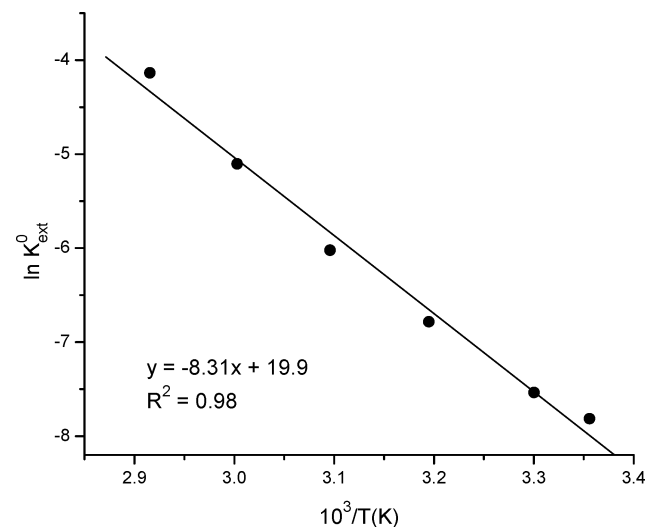


Figure 4. Determination of ΔH . Conditions: $[\text{Fe}^{3+}]_{\text{aqueous}} = 0.80 \text{ M}$, $[\text{CYANEX 272} + \text{TBP}]_{\text{organic}} = 30\% + 30\%$ (v/v in ESCAID 110, initially neutralized to 15% with respect to CYANEX 272), equilibrium pH = 1.2, $T = 298, 303, 313, 323, 333, 343 \text{ K}$, $\text{A/O} = 1$, $t = 5 \text{ min}$.

Table 2. Removal of Iron from the Leaching Solution in Different Numbers of Countercurrent Extraction Stages^a

initial conc of metals (g L ⁻¹)		no. of stages	conc of metals (g L ⁻¹) in the leaching solution after extraction	
Fe	Zn		Fe	Zn
43.1	13.6	3	7.70	12.8
		4	3.05	12.5
		5	1.01	12.1
		6	0.09	11.6

^a Extractant solution = 30% CYANEX 272 + 30% TBP, equilibrium pH = 1.2, $\text{A/O} = 0.5$, $T = 323 \text{ K}$, $t = 15 \text{ min}$.

Na^+ ions, released during the above mass transfer, further react with the available dimer $(\text{HR})_2$ to form NaR (eq 2), thus propagating the extraction process until the maximum loading of the extractant is achieved. The data, plotted in Figure 1, suggest that the mixture of 30% (v/v) CYANEX 272 + 30% TBP (v/v) could extract around 48% of the initial 0.80 M Fe^{3+} . These values, in molar terms, imply that 1.1 M (initial extractant concentration) of CYANEX 272 can load 0.38 M of the metal ion. An extractant solution containing 30% (v/v)

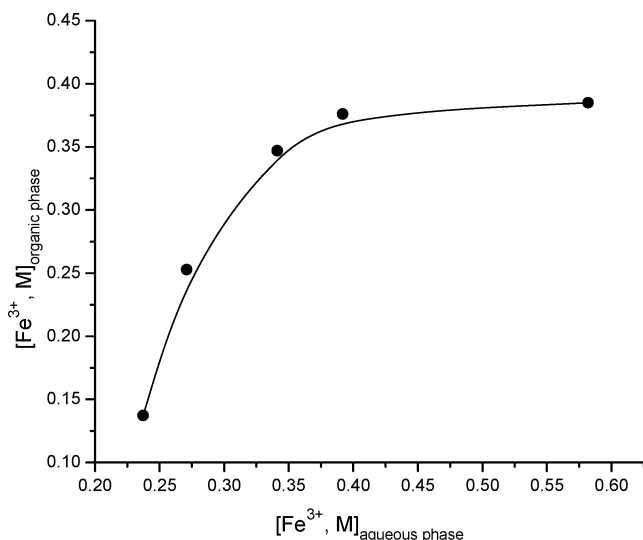


Figure 5. Extraction isotherm of Fe^{3+} . Conditions: $[\text{Fe}^{3+}]_{\text{initial in aqueous}} = 0.80 \text{ M}$, $[\text{CYANEX 272} + \text{TBP}]_{\text{organic}} = 30\% + 30\%$ (v/v in ESCAID 110, initially neutralized to 15% with respect to CYANEX 272), equilibrium $\text{pH} = 1.2$, $T = 323 \text{ K}$, $t = 15 \text{ min}$.

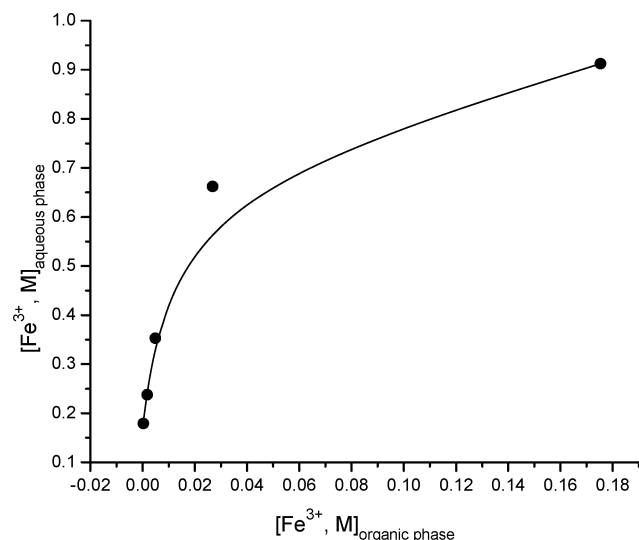


Figure 6. Stripping isotherm of Fe^{3+} . Conditions: $[\text{Fe}^{3+}]_{\text{organic}} = 0.38 \text{ M}$, $[\text{CYANEX 272} + \text{TBP}]_{\text{organic}} = 30\% + 30\%$ (v/v in ESCAID 110, initially neutralized to 15% with respect to CYANEX 272), stripping reagent = $2 \text{ M H}_2\text{SO}_4$, $T = 323 \text{ K}$, $t = 10 \text{ min}$.

CYANEX 272 and 30% TBP (v/v) (initially neutralized to 15% with respect to CYANEX 272) was used in all subsequent experiments.

The variation in the extraction of Fe^{3+} against the equilibrium pH of the aqueous phase is shown in Figure 2. The transfer of the metal ion in the extractant phase increases with the increasing pH of the aqueous medium, thus indicating an exchange of cations during the process. It reaches the maximum ($\approx 48\%$) at pH around 1.2.

The contribution of TBP in the process of Fe^{3+} extraction with CYANEX 272 has been explained in Figure 2. The related experiment was done using lower concentrations of the metal ion (0.08 M Fe^{3+}) and the extractant (3% v/v CYANEX 272 or 3% v/v CYANEX 272 + 3% v/v TBP) to prevent any instance of crud formation. The ratio of the metal to the extractant was still the similar to that in all other studies. Besides improving the phase separation characteristics, TBP helps in achieving the extraction of Fe^{3+} at relatively low pH values.

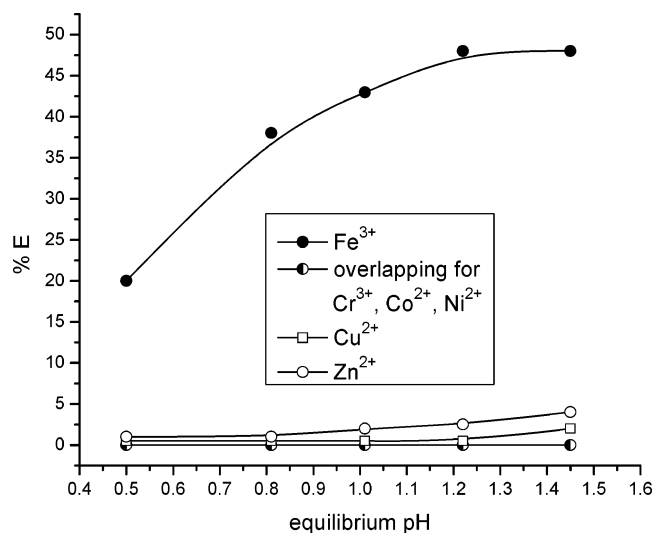


Figure 7. Extraction of Fe^{3+} in the presence of Cr^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} . Conditions: $[\text{Fe}^{3+}]_{\text{aqueous}} = 0.80 \text{ M}$, $[\text{Cr}^{3+}$, Co^{2+} , Ni^{2+} , Cu^{2+} , and $\text{Zn}^{2+}]_{\text{aqueous}} = 0.25 \text{ M}$, $[\text{CYANEX 272} + \text{TBP}]_{\text{organic}} = 30\% + 30\%$ (v/v in ESCAID 110, initially neutralized to 15% with respect to CYANEX 272), $T = 323 \text{ K}$, $\text{A/O} = 1$, $t = 15 \text{ min}$.

3. Determination of the Thermodynamic Equilibrium Constant for the Fe^{3+} Extraction Reaction. Considering the nonideality of the aqueous phase, the thermodynamic extraction constant " K_{ext}^0 " and the distribution ratio " D " for eq 17 can be given as

$$K_{\text{ext}}^0 = \frac{c_{\text{FeR}_3} a_{\text{Na}^+}^3}{a_{\text{Fe}^{3+}} c_{\text{NaR}}} \quad (18)$$

$$D = \frac{c_{\text{FeR}_3}}{a_{\text{Fe}^{3+}}} \quad (19)$$

Rearranging the relations 18 and 19 gives eq 20

$$\log (Da_{\text{Na}^+}^3) = \log K_{\text{ext}}^0 + 3 \log c_{\text{NaR}} \quad (20)$$

As suggested by eq 20, the value of intercept in a graphical representation of $\log (Da_{\text{Na}^+}^3)$ vs $\log [\text{NaR}]_{\text{Free}}$ or $\log [\text{R}^-]_{\text{Free}}$ (since Na^+ ions do not participate in the complex formation and are ultimately released in the aqueous solution) would evaluate the constant K_{ext}^0 . This necessary plotting of data has been shown in Figure 3. Some of the required data was calculated as follows:

$$\begin{aligned} [\text{R}^-]_{\text{Free}} &= [\text{R}^-]_{\text{Initial}} \text{ (determined considering extractant dimerization)} - \\ &[\text{R}^-]_{\text{Complexed}} \text{ (determined by \%E)}, \quad a_{\text{Na}^+} = [\text{Na}^+] \gamma_{\text{Na}^+}, \\ a_{\text{H}^+} &= [\text{H}^+] \gamma_{\text{H}^+}. \end{aligned}$$

Under the taken experimental conditions, the value of K_{ext}^0 for the extraction reaction (eq 17) is found to be 1.8×10^{-2} (from Figure 3).

4. Extraction Kinetics: Effect of Temperature. The effect of the temperature on the extraction of 0.80 M Fe^{3+} (equilibrium $\text{pH} = 1.2$) with 30% CYANEX 272 + 30% TBP ($\text{A/O} = 1$) was recorded for different time intervals (5–60 min). At room temperature (298 K), a contact time of 45–50 min was required for achieving the equilibrium transfer ($\approx 48\%$) of Fe^{3+} into the organic phase. An increase in the reaction temperature improved

Table 3. Representation of a Six-Stage Countercurrent Extraction of Fe³⁺ from the Leaching Solution^a

		Stages							
		1	2	3	4	5	6		
loaded extractant	Fe	21.5	21.0	18.9	15.0	9.8	2.6	fresh extractant	
	Zn	1.0	0.95	0.8	0.6	0.4	0.2		
	Cu	0.01	0.01	0.01	0.01	0.01	0.01		
aqueous feed	Fe	42.1	37.9	30.1	19.7	5.3	0.09	aqueous raffinate	Fe
	Zn	13.5	13.2	12.8	12.4	12.0	11.6		Zn
	Cu	0.31	0.31	0.31	0.30	0.30	0.30		Cu
									0.09
									11.6
									0.30
									0.30

^a Extractant solution = 30% CYANEX 272 + 30% TBP, equilibrium pH = 1.2, A/O = 0.5, $T = 323$ K, $t = 15$ min. Note: metal concentrations are given in grams per liter.

Table 4. Recovery of Iron from the Loaded Organic Phase after Its Extraction from the Leaching Solution of a Zinc Concentrate: Composition of Metals in the Recovered Aqueous Phases after Scrubbing and Stripping Stages^a

conc of metals (g L ⁻¹) in the organic phase			conc of metals (g L ⁻¹) in the recovered aqueous phase after two-stage scrubbing with 0.20 M H ₂ SO ₄			conc of metals (g L ⁻¹) in the recovered aqueous phase after two-stage stripping with 2 M H ₂ SO ₄		
Fe	Zn	Cu	Fe	Zn	Cu	Fe	Zn	Cu
21.5	1.0	0.01	0.1	4.9	0.05	21.1	0.1	<0.01

^a Scrubbing: 0.20 M H₂SO₄, A/O = 0.2, $T = 323$ K, $t = 10$ min. Stripping: 2 M H₂SO₄, A/O = 1, $T = 323$ K, $t = 10$ min.

the rate of mass transfer. A reasonably acceptable rate (<15 min) of the equilibrium mass transfer, for example in the case of a mixer–settler setup, could be achieved beyond 323 K.

In another experiment, the extraction of Fe³⁺ was again performed as a function of varying reaction temperature (298–343 K), but keeping the equilibration time constant to 5 min. The values of the distribution ratio D were determined and then used to calculate K_{ext}^0 according to eq 20. The following data is obtained: $K_{\text{ext}}^0 = 4.03 \times 10^{-4}$ (298 K), 5.33×10^{-4} (303 K), 1.13×10^{-3} (313 K), 2.42×10^{-3} (323 K), 6.07×10^{-3} (333 K), and 1.60×10^{-2} (343 K). These values of K_{ext}^0 have been used in a graphical representation ($10^3/T$ vs $\ln K_{\text{ext}}^0$; Figure 4) of the Van't Hoff relation $-\ln K_{\text{ext}}^0 = \Delta H/RT$ to determine the heat of reaction (ΔH). A linear curve is observed with the slope of 8.31, which estimates ΔH ($\Delta H = 2.303R$ slope) to be 159 kJ mol⁻¹.

5. Loading Capacity of the Extractant Solution and Assessment of the Extraction Stages. Figure 5 shows a distribution isotherm obtained for the extraction of Fe³⁺ upon varying the volume ratio (2, 1, 0.75, 0.5, and 0.25) of the aqueous to the organic phase. Evidently, 30% CYANEX 272 (i.e., 1.1 M CYANEX 272) can load a maximum of 0.38 M Fe³⁺. These results are in agreement of the data obtained in section 2 (Fe³⁺ Extraction as a Function of Extractant Composition and Equilibrium pH), wherein the same loading capacity (34%) has been observed.

Unlike a typical McCabe–Thiele diagram, the isotherm shown in Figure 5 cannot be used to evaluate the required number of Fe³⁺ extraction stages, if the desired recovery is more than 99%. Such an evaluation has, therefore, been made through

some multistage continuous countercurrent laboratory scale experiments selecting an aqueous to organic phase ratio of 0.5. The results of this study are given in Table 2. Six stages of the extraction are required to transfer more than 99% of the initial Fe³⁺ into the the organic phase.

6. Stripping Studies. Some preliminary studies highlighted satisfactory stripping results with the use of 2 M H₂SO₄ as a reagent (Fe³⁺ in the organic phase = 0.38 M). Extending the study, the effects of the temperature and the A/O ratio on the stripping have been investigated. An increase in the temperature favors the kinetics of back extraction. At 298 K, the achievement of an equilibrium state (99.5% stripping) took 25 min. This rate of the stripping improved under the influence of increasing temperature, e.g., 20–22 min at 303 K, 15–17 min at 313 K, 10–12 min at 323 K, 5–6 min at 333 K.

The stripping isotherm (A/O ratio = 2, 1.5, 1, 0.5, 0.2) has been shown in Figure 6. The plot is useful for determining the number of stages that would be required to achieve a certain degree of the metal concentration in the stripping liquor. However, the number of stripping stages required for regenerating the organic phase (more than 99% removal of the metal ion from the organic phase) is difficult to simulate. In a separate experiment, some continuous countercurrent experiments have revealed that two stages of the stripping (A/O ratio = 1) back extract around 99.5% of 0.38 M Fe³⁺.

7. Selectivity of Fe³⁺ Extraction over Some Associated Metal Ions. The occurrence of iron as an impurity in leach solutions is a major problem in the hydrometallurgy of various base metals, such as chromium, cobalt, nickel, copper, and zinc. Some studies have, therefore, been included to test the selectivity

of the present Fe^{3+} extraction system toward 0.25 M Cr^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} using a synthetic mixture containing all the mentioned metal ions. The results (Figure 7) exhibit a negligible extraction of Cr^{3+} , Co^{2+} , Ni^{2+} , and Cu^{2+} over the entire investigated pH range. The extraction of Zn^{2+} remains at 2–3%. These observations highlight an excellent selectivity of the proposed Fe^{3+} extraction system.

As indicated, Zn^{2+} co-extracts with Fe^{3+} to an extent of 2–3%. In some of the cases, even this amount of the co-extraction may lead to an objectionable buildup during the multistage extraction steps. This buildup would need to be scrubbed before the Fe^{3+} stripping step. Some experiments have concluded that two-stage scrubbing with 0.20 M H_2SO_4 (A/O = 0.2) can be used for the quantitative removal of the co-extracted Zn^{2+} without any significant loss of Fe^{3+} .

8. Application of the Proposed Extraction Process. The authors' research team is currently involved in another industry (Somincor, Portugal) sponsored project, dealing with the recovery of various metals from a zinc concentrate, mined from the Neves-Corvo mine. This matrix has the following composition: 36% Zn, 36% S, 2% Fe, and 4% Cu. Minor metals include In (0.02%), Ag (0.01%), Pb (0.84%), As (7 g/t), Hg (0.4–1 g/t), Sb (0.5 g/t), Tl (0.2 g/t), and Bi (50 g/t). As a part of the above project, the zinc concentrate was subjected to the atmospheric oxidative leaching with a reagent mixture of 0.40 M $\text{Fe}_2(\text{SO}_4)_3$ and 0.50 M H_2SO_4 . The final leach liquor contained a high amount of the iron impurity. This leach liquor has been subjected to the present Fe^{3+} extraction system for the purification from iron. The detailed procedure is given below:

A 50 mL aliquot of the leaching solution at an initial pH = 1.2 was contacted in a six-stage countercurrent extraction setup with a mixture of 30% CYANEX 272 and 30% TBP (initially neutralized to 15% with respect to CYANEX 272) (A/O = 0.5) maintaining the equilibrium pH of 1.2. A schematic representation of the scheme, along with the changes in the concentrations of the metal ions during the different stages of the experiment, is given in Table 3. After the completion of the experiment, total iron in the leaching solution was less than 0.1 g L^{-1} , thus depicting more than 99% decontamination of the aqueous phase from the iron impurity. Around 15% of the initial zinc was lost as a result of co-extraction, which was subsequently recovered by scrubbing the organic phase with 0.20 M H_2SO_4 (A/O = 0.2) (Table 4). The extracted Fe^{3+} was then stripped from the organic phase in two stages using 2 M H_2SO_4 (A/O = 1). The data, given in Tables 3 and 4, indicate that the treated leaching solution is free from the iron impurity and the recovered iron solution is reasonably pure as well. The aqueous phases, obtained as a result of extraction, scrubbing, and stripping cycles, contain pure metal solutions that should be usable in further treatment circuits.

Conclusions

The present study establishes CYANEX 272 as an extractant for a macro level concentration of Fe^{3+} . An equivolume addition of TBP in the extractant solution is required to attain satisfactory phase separation characteristics. The proposed extractant mixture extracts Fe^{3+} over a fairly wide range of the aqueous phase pH with a good loading capacity. Speciation studies have ascertained the mechanism of the iron extraction under the test conditions, i.e., Fe^{3+} = 0.80 M, pH = 1.2. The speciation data have also contributed to the determination of other physical parameters, namely the stoichiometry of the extracted complex, the thermodynamic extraction constant, and the heat of reaction. The

extraction process is endothermic in nature and an acceptable rate of mass transfer can be achieved at a reaction temperature of 323 K. The stripping of the extracted metal ion is easily achieved using 2 M H_2SO_4 , which can be cited as one of the biggest advantages of the proposed extraction system over DEHPA and Ionquest 801 extractants. The extractant solution also provides a fair selectivity to the extraction of Fe^{3+} in the presence of some commonly associated metals, namely Cr^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} . An overall usefulness of the outlined extraction system has been verified by decontaminating the leaching solution of a zinc concentrate. As an added advantage, the recovered iron solution is pure and reasonably concentrated. This recovered solution can be used to form some marketable product such as water treatment reagents or iron oxide. It may be useful to point out here that each aliquot of the extractant solution, used during the course of the present study, was regenerated (scrubbed, stripped, and washed with water) five times. Use of the regenerated extractant solution in the extraction studies did not change the results.

Extraction of Fe^{3+} from dilute aqueous solution is reported elsewhere.^{18,19} In comparative terms, it can be highlighted that the mechanism of extraction in concentrated iron solutions is different than in dilute solutions due to change of aqueous phase speciation. The use of a modifier is required in the case of concentrated solutions, which also provides a kind of synergist effect in the extraction. The selectivity of CYANEX 272 for Fe^{3+} has been investigated for a wider variety of associated metals, and the proposed method has been applied to an industrial leach liquor of a much complex composition.

As already highlighted, one of the major advantages of the proposed Fe^{3+} extraction system is the convenient regeneration of the applied extractant solution. The selectivity of system is also a point to be noted. Since the current trends in metallurgy talk about waste minimization, plus process economics, the present work targets the recovery of iron, rather than its removal and disposal.

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Notations

- \bar{a} = hard core ion diameter, Å
- A_ϕ, b = constants in the equation of Debye–Hückel limiting law slope, $(\text{mol kg}^{-1})^{1/2}$
- A_γ = constants in the Debye–Hückel equation, $(\text{mol kg}^{-1})^{1/2}$
- C_{ij}^Φ = solute specific parameters in the Pitzer equation
- $B_{Ma}, B_{cX}, B'_{Ma}, B'_{cX}$ = short-range binary interaction parameters in the Pitzer equation, $\text{mol}^{-1} \text{ kg}$
- C_{Ma}, C_{cX} = ternary interaction parameters in the Pitzer equation, $\text{mol}^{-2} \text{ kg}^2$
- D = distribution ratio
- E = equivalent molality of the solution, mol kg^{-1}
- %E = extraction percentage
- f' = Debye–Hückel limiting law slope
- I = ionic strength of the solution, mol kg^{-1}
- ΔH = heat of reaction, kJ mol^{-1}
- K_d = dissociation constant of the acid
- K_i^0 = thermodynamic equilibrium constant
- K_i^c = apparent equilibrium constant

K_{ext}^0 = thermodynamic extraction constant

m_i = molality of species i , mol kg⁻¹

M, c, c' = cations in the solution

R = gas constant, 8.314 J mol⁻¹ K⁻¹

t = time

T = absolute temperature, K

X, a, a' = anions in the solution

z_i = ionic charge

Greek Letters

β = constant in the Debye–Hückel equation, (mol kg⁻¹)^{1/2}

$\beta_{ij}^0, \beta_{ij}^1$ = solute specific parameters in the Pitzer equation

γ_i = activity coefficient of species i

Θ_{ij} = binary interaction of the similarly charged ions

ψ_{ijk} = ternary interaction of the two similarly charged ions with an ion of opposite charge

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