

Equilibrium and rate of iron(III) extraction from chloride solutions by individual hydrophobic extractants and their mixtures

Katarzyna Staszak¹, Ryszard Cierpiszewski², Krystyna Prochaska^{1*}

¹Poznan University of Technology, Institute of Chemical Technology and Engineering, pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland, e-mail: Krystyna.Prochaska@put.poznan.pl,

²Poznan University of Economics, Faculty of Commodity Science, al. Niepodległości 10, 61-875 Poznań, Poland,

The main goal of this work was to study and compare the rate of iron(III) extraction from chloride solutions by commercial extractants: Alamine 336, TOPO and LIX 54 and their mixtures. Using the interfacial tension data, obtained for mixed systems, the values of surface mole fraction and molecular interaction parameter of extractants were estimated. Determination of the extraction rates was performed by using the Lewis-type stirred transfer cell. It was found that the extraction efficiency of extractants are changed in the following order: Alamine 336 > TOPO > β -diketone. The addition of a chelating extractant to the system decreases the extraction efficiency, for example the addition of β -diketone to TOPO decreases the extraction efficiency by about 50%.

Keywords: extraction, iron(III), Alamine 336, TOPO, β -diketone.

INTRODUCTION

Iron is a naturally occurring element that also enters the environment from industrial sources. The *EC Drinking Water Directive* (98/83/EEC) lists iron as the indicator parameter in Part C at the maximum permissible value of 0.2 mg/L. In the former Directive (80/778/EEC) a guide value, the level considered to be ideal, had been set at 0.05 mg/L. In Poland after acceding to European Union the maximum permissible value of iron in the water has been changed from 0.5 to 0.2 mg/L.

Solvent extraction is usually applied the separation and/or concentration of valuable metals. Iron is commonly found in the aqueous solutions in the case of the recovery of non-ferrous metals by hydrometallurgical processes, accompanying all these metals. In the world's hydrometallurgical process nearly 18 million ton/year of iron are produced. Moreover, removal of iron from aqueous wastes is also very important from the ecological point of view, especially after mentioning the above change of the standard for iron in the water in Poland. Commercially available organophosphorous extractants can be employed to remove iron in some hydrometallurgical processes. Among neutral extractants, tributylphosphate (TBP)¹ and methyl *iso*-butyl ketone (MIBK)² have been used extensively for the extraction of iron(III) from hydrochloric acid solutions. Organophosphorus acid derivatives such as di-2-ethylhexylphosphoric acid (DEHPA)³⁻⁵ or amines^{6,7} have also been used. All these extractants have their own drawbacks: MIBK has a low flash point and high solubility in the aqueous phase; the use of TBP usually leads to the third phase formation; a high acid concentration is required to strip iron(III) from the acidic extractants such as DEHPA³. Thus, the development of new extraction systems for the extraction of iron(III) seems to be very important.

The aim of this work was to investigate the rate of iron(III) extraction from chloride solutions by three commercial extractants: trioctylphosphine oxide (TOPO), Alamine 336 with trialkylamine (C₃:C₁₀=2:1) as an active substance and LIX 54 with 1-phenyldecane-1,3-dione as active substance and their mixtures. Assuming that the

complexation of iron(III) in the considered systems probably occur at the interface, the adsorption properties of the extractants at the hydrocarbon/water interface were also studied.

EXPERIMENTAL

TOPO, LIX 54 and Alamine 336 were used as extractants. Only TOPO was a pure compound. The others were commercial reagents and used as delivered. Toluene and low aromatic kerosene Exxsol D220/230 (Deutsche Exxon Chemical, ESSO A.G.) were used as organic diluents. The concentration of the extractants was changed from 30% to 100% v/v.

The extraction was carried out in separatory funnels using the same volumes (10 cm³) of both phases. The phases were mechanically shaken for 1 hour and then allowed to phase separate (usually more than 1 hour). Demineralized water (10 cm³) was used for stripping.

The kinetics of iron extraction was investigated using a constant interfacial area Lewis-type cell (21°C). The handmade apparatus provided a constant interfacial area of 16.6 cm², volume of aqueous or organic phase was equal to 95 cm³. Samples of organic phases (1 cm³) were withdrawn after appropriate periods of time. The sample of the organic phase was stirred with 10 cm³ of water and the iron concentration in the aqueous phase was determined. Fresh organic solution (1 cm³) was added to the stirred cell to maintain a constant volume ratio. The stirrer speeds in the organic and aqueous solutions were kept in the range of 30 – 150 rpm to maintain a flat and stable interface.

The concentration of iron was determined in the aqueous phase before and after extraction and after stripping for equilibrium experiments. For kinetics experiments iron concentration was measured only after stripping, as was mentioned above. The concentration of iron was determined by atomic absorption spectroscopy using a Varian SPECTR AA800. The measurements were carried out at 248.3 nm, with a relative error of analysis less than 3%.

The FTIR spectra were recorded at 2 cm⁻¹ resolution using a Bruker IFS 113v spectrometer (range of 4000 –

500 cm^{-1}). Spectra for the individual species were run in the liquid film or in the KBr disk, for the mixed systems in chloroform solution with the total concentration 10^{-1} mol/L.

The interfacial tension was measured by the drop volume method with a Lauda TVT1 tensiometer with an experimental error of 0.1 mN/m. The measurements were carried out at $21 \pm 0.1^\circ\text{C}$ with pre-saturated phases (by automatically shaking for 5 hrs). Freshly distilled toluene (POCh S.A.) and re-distilled water were used in preparation the solutions.

RESULTS AND DISCUSSION

The iron(III) extraction from chloride acidic solutions with different concentrations of HCl in five systems were investigated. Three systems with individual extractant (Alamine 336, TOPO, LIX 54) as well as two systems with equimolar mixture of TOPO with Alamine 336 or LIX 54 were considered. The obtained results are presented in Figure 1. The high efficiency for iron(III) extraction of considered reagents was demonstrated by the extraction isotherms presented for 0.1 M solutions of TOPO and Alamine 336 in toluene. Solutions of TOPO and Alamine 336 were loaded up to 2.67 and 2.51 g/L Fe(III), respectively. However the mixture of these compounds or TOPO/LIX 54 extracted less iron(III) than the individual reagents. The chelating extractant did not extract iron(III) from hydrochloric acid solutions. Only a small amount of iron(III) was extracted in this case.

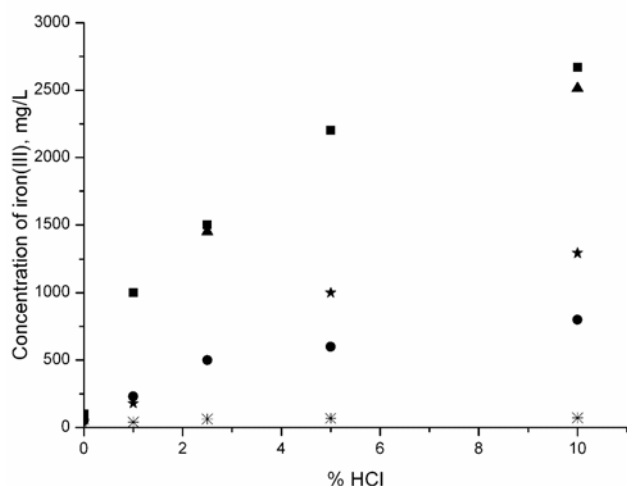


Figure 1. Extraction of iron(III) from hydrochloric acid solution (initial concentration of Fe(III) 5g/L, concentration of extractants – 0.1 M in toluene, ALAMINE[®]336(■), TOPO(▲), ALAMINE[®]336 + TOPO (●), TOPO+ LIX 54 (★), ALAMINE[®]336 in Exxsol D220/230 (*))

Extraction of Fe(III) by TOPO and Alamine 336 increased significantly as the concentration of neutral iron(III) chloride and HCl increased. For instance, in the 10% HCl, the mole fractions of Fe(III) chlorocomplexes were estimated approximately to be 0.18, 0.49, 0.26 and 0.08 for FeCl_3 , FeCl_3^{2+} , FeCl_4^- and Fe^{3+} , respectively⁸. These cationic species would not be extracted with either the solvating or basic reagents. It can be assumed that in the case of Fe(III) extraction from acid chloride solutions the molecules of extractants can react only with the

chlorocomplex FeCl_3 . The molar fraction of FeCl_3 in the aqueous phase depends on the chloride concentration and on the ionic strength (Figure 2) and as shown the molar fraction of this complex increases when the chloride concentration rises. The estimated values of molar fractions are in good agreement with the results presented by Biswas and Begun⁹. The solvating (S) and basic (B) reagents could extract the neutral iron(III) chlorocomplex according to the reactions: $\text{FeCl}_{3w} + 2\text{S}_o = \text{FeCl}_3 \cdot 2\text{S}_o$ and $\text{FeCl}_{3w} + \text{B} \cdot \text{HCl}_o = (\text{BH})\text{FeCl}_4_o$.

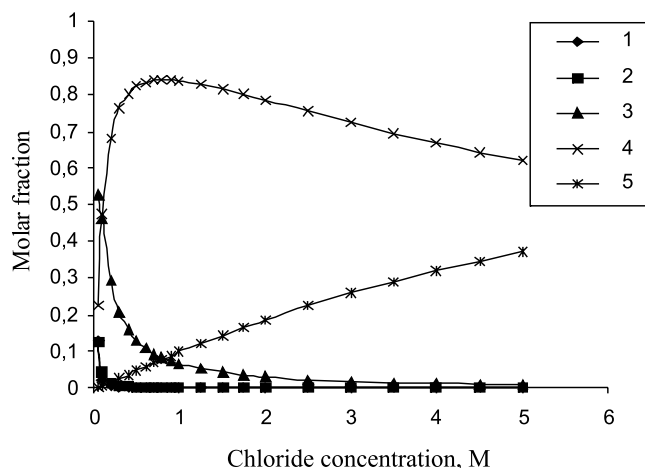


Figure 2. Influence of chloride concentration on molar fractions of FeCl_3^{3-} in the aqueous phase ([Fe(III)] – 0,01 M, 1 – Fe^{3+} , 2 – FeCl_3^{2+} , 3 – FeCl_4^- , 4 – FeCl_3 , 5 – FeCl_4^-)

In Figure 3 the results of kinetics of iron extraction procedure are shown for system containing a mixture of LIX 54 and TOPO. The concentration of Fe(III) in the organic phase increases almost linearly with time from zero up to about 40 minutes. The slopes of linear relations were used to determine the fluxes of iron transfer from the aqueous to the organic phase. The initial extraction rates estimated for the considered systems are shown in Table 1 (the initial concentration 5 g/L of iron). These results indicated that the initial extraction rate is approximately proportional to the speed in the range from 30 to 120 rpm. Under 150 rpm the interface becomes unstable and the extraction increases very fast. On this basis, 90

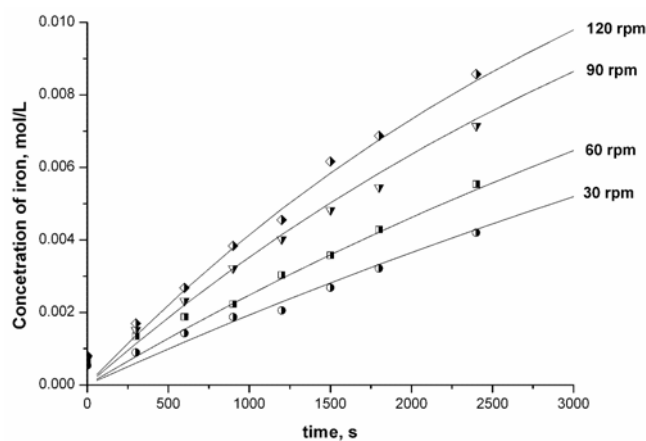


Figure 3. Effect of the stirring speed on the initial rate of the extraction of iron(III) by 0.05 M TOPO and 0.05 M LIX54 in toluene; aqueous phase: 5g/L Fe(III), HCl; stirring speed: (●) 180 rpm, (▼)140 rpm, (■) 90 rpm, (◆) 60 rpm

Table 1. Initial rate of iron extraction

Extractant	Initial rate of extraction $r \times 10^6$ [mol/dm ² s]			
	30	60	90	120
rpm	30	60	90	120
ALAMINE 336 in toluene	198	730	1580	2180
ALAMINE 336 and TOPO(1:1 mol/mol) in toluene	32.9	80	91.3	210
TOPO toluene	140	871	1290	1500
TOPO + LIX 54 (1:1 mol/mol) toluene	130	907	1230	1430
LIX54 toluene		52	59	65
ALAMINE 336 in Exxsol D220/230	0	4.6	5.5	6.8

rpm was selected for the study of the interfacial phenomena due to the very good stability of the interfacial surface and high extraction rate. The best results were obtained for the system containing Alamine 336 in toluene, where the rate of extraction is almost 20% higher in comparison to the results with TOPO (the initial rate at 60 rpm was lower than expected but additional experiments were not done). The addition of a second extractant led to a significant decrease in the initial rate of extraction. Moreover, it was found that the rate of Fe(III) transport from acidic water solution to the organic phase by using LIX 54 is very slow in comparison to the system with TOPO or Alamine 336. The results obtained in the systems with toluene are much higher in comparison to the systems where Exxsol D220/230 was used as a diluent. Good agreement between the rate of extraction and equilibrium of extraction was observed.

Effect of iron(III) concentration on the initial extraction rate was also studied in our previous paper¹⁰. The obtained results show that the rate of extraction is affected by the concentration of iron(III) and as was stated the rate of extraction increases with the increase of the concentration of metal ions in the system.

Mass transfer of Fe(III) between an aqueous and an organic phase (k_l) was also studied, too. The experimental mass transfer coefficients can be expressed by the equation:

$$k_l = \frac{V_1 \ln \frac{C_1^0}{C_1}}{At} \quad (1)$$

where: A – area of interface, V volume of phase, C – concentration. The obtained results are shown in Table 2.

According to Bandyopadhyay et. al.¹¹ the best model of calculation of mass transfer coefficients for extraction can be obtained by using the following correlation:

$$\frac{k_l L}{D} = 0.187 S_{C_1}^{0.33} Re^{0.97} \left(\frac{\mu_2}{\mu_1} \right)^{1.6} \left(1 + \frac{Re_c \mu_2}{Re \mu_1} \right) \quad (2)$$

A comparison between the experimental mass transfer coefficients and the values of k_l calculated from the above correlation are in good agreement, especially in the region of high speed of the stirrer rotation (Table 2).

Table 2. Experimental and predicted mass transfer coefficients, m/s·10⁶

	60 rpm	90 rpm
ALAMINE 336	0.487	2.17
ALAMINE 336 + TOPO	0.243	0.444
Bandyopadhyay's equation	0.691	2.01

Modeling of the mass transfer in a Lewis cell

The concentration of metal ions in the aqueous and organic phase can be evaluated by the following equations¹²:

$$a) V_w \frac{dC_w(t)}{dt} = k \cdot S \left(C_w(t) - \frac{C_o(t)}{D} \right) \text{ in the aqueous phase: } \quad (3)$$

$$b) V_o \frac{dC_o(t)}{dt} = k \cdot S \left(C_w(t) - \frac{C_o(t)}{D} \right) \text{ in the organic phase: } \quad (4)$$

where: C – concentration of metal, D – distribution coefficient, A – interfacial surface, V – phase volume, t – time, "0" – initial value. Rearranging both equation gives the time dependent for metal ions concentrations. The correlation finally can be expressed in the following forms:

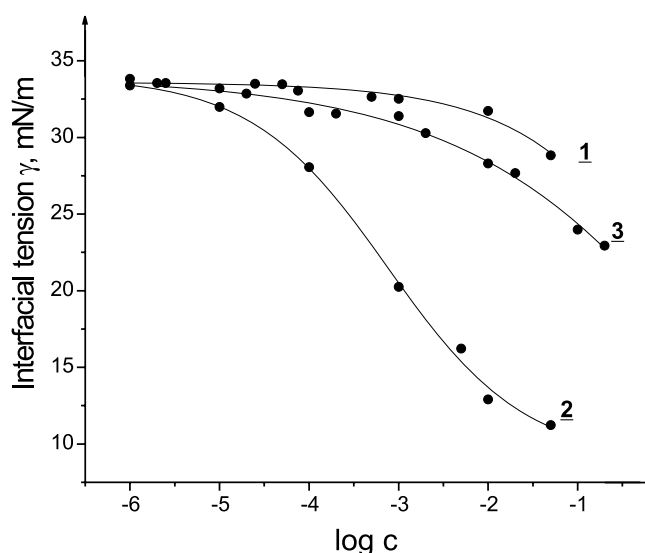
$$C_w(t) = \frac{C_o^0 V_o + C_w^0 V_w + V_o (DC_w^0 - C_o^0)}{DV_o + V_w} \exp\left(-\frac{k \cdot t \cdot S (DV_o + V_w)}{DV_o V_w}\right) \quad (5)$$

$$C_o(t) = \frac{D(C_o^0 V_o + C_w^0 V_w) - V_o (DC_w^0 - C_o^0)}{DV_o + V_w} \exp\left(-\frac{k \cdot t \cdot S (DV_o + V_w)}{DV_o V_w}\right) \quad (6)$$

A good agreement was obtained for the concentration of metal ions between the experimental and correlated values (Figure 2). The correlation coefficients which equal 0.994, 0.996, 0.998, 0.996 for the speed in the range from 30 to 120 rpm were calculated, respectively, for the proposed model.

Adsorption Properties

The interfacial tension isotherms for investigated extractants are illustrated in Figure 4 a and b. The estimated values of X_i and β (estimated from the Rosen equation¹³) are presented in Table 3. TOPO lowers the interfacial tension more effectively and forms a more densely populated monolayer than LIX 54. The values of Γ^∞ (calculated from the Szyszkowski equation¹³) are equal to $1.14 \cdot 10^{-6}$ mol/m² and $0.30 \cdot 10^{-6}$ for TOPO and LIX 54. In spite of the obvious different interfacial activities of these two compounds the composition of the mixed adsorbed monolayer and the bulk organic phase are very close. The values of X_{TOPO} decrease insignificantly when the interfacial tension increases, however the mean value is close to 0.4.

**Figure 4a.** Interfacial tension isotherms for TOPO (2), LIX 54 (1) and equimolar mixture TOPO+LIX54 (3) in water/toluene system

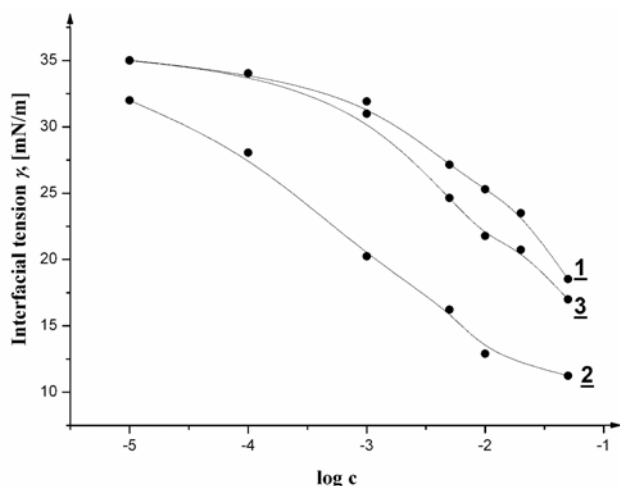


Figure 4b. Interfacial tension isotherms for TOPO (2), Alamine 336 (1) and equimolar mixture (3) in water/toluene system, c in mol/dm³

Table 3. Values of surface mole fraction X_{TOPO} and molecular interaction parameter β in the toluene/water system

γ [mN/m]	X_{TOPO}	β	γ [mN/m]	X_{TOPO}	β
TOPO/ β -diketone			TOPO/Alamine 336		
30	0.46	2.07	32	0.27	4.02
32	0.42	2.47	28	0.29	3.61
33	0.40	2.46	24	0.30	3.30

The assumption that the molecules of TOPO and LIX 54 interact with each other seems to be rather improbable. The obtained values of β (Table 3) indicate a clearly repulsive interaction between the adsorbed molecules of these extractants in a mixed monolayer formed at the toluene/water interface. If these extractants do not interact with each other then the characteristic stretching vibrations of the P=O group for TOPO should be visible in the FT-IR spectra for the binary mixture of TOPO and LIX 54. This effect is illustrated in the FT-IR spectra in which absorption bands in the P=O stretching region are shown for the individual TOPO molecules and for the mixtures in the 1145 and 1144 cm⁻¹ regions, respectively. Thus, the formation of the intermolecular hydrogen bonds between the carbonyl groups of LIX 54 and the phosphoryl group of TOPO is rather improbable because of the presence of the free P=O stretching vibration bands in the spectra of the binary mixtures.

As it was mentioned above the addition of LIX 54 to TOPO decreases the extraction efficiency by about 50%. Moreover, in the considered mixture the extractant which has the less extraction efficiency dominated at the interface. Probably the effect of the decreasing extraction efficiency could be explained by the different structure of the adsorbed mixed monolayer with the lower presence of TOPO at the saturated interface, not by an interaction between the reagents.

It was found that the TOPO decreased the interfacial tension at the toluene/water interface much more effectively than Alamine 336. In the light of the above, it seems rather surprising that the molecules of TOPO do not occupy a dominant position at the mixed adsorbed monolayer. The values of the surface mole fraction of Alamine 336 vary in the range from 0.68 to 0.73. The obtained

results proba could be explained in terms of different hydrophilicities of extractants in both considered mixtures. The conclusions presented above are in complete agreement with the results of our earlier study of the co-adsorption in the systems with TOPO/TBP described previously¹³. The content of TOPO at the saturated mixed adsorbed monolayer was surprisingly small too. In the case of the mixture of TOPO/Alamine 336 the molecular interaction in a mixed adsorbed monolayer should not be neglected. Positive and high values of the parameter β indicate strong repulsive interaction among the molecules extractants adsorbed in the mixed monolayer. The FT-IR spectra of trioctylamine (TOA) (i.e. the active substance of Alamine 336 reagent) and the mixture with TOPO are presented in Figure 5. As it was mentioned above the characteristics for phosphine oxide stretching vibration P=O are observed in the region 1150 – 1100 cm⁻¹. Similar to the mixed system TOPO/LIX 54, in the case of mixture of TOPO and TOA the characteristic absorption bands in the P=O stretching region is moved from 1145 to 1144 cm⁻¹ regions for individual TOPO molecules and for mixtures, respectively. The presence of this band indicate the lack of interaction between molecules of extractants in the investigated mixed system.

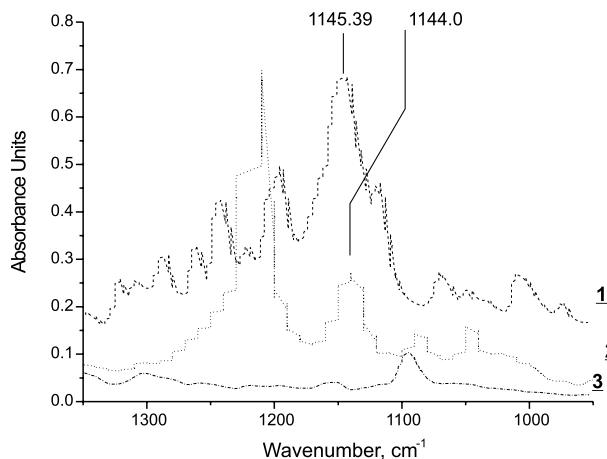


Figure 5. The FT-IR spectra of TOPO (1), TOA (2) and their equimolar binary mixture in chloroform solution (3) in the stretching region of P=O and P-O-C(aliph), technique KBr 0.2mm

The values of diffusion coefficients D (estimated from the Ward-Tordai equation¹⁴) according to the dynamic interfacial measurements are presented in Table 4. Taking into account the above results it should be expected that the diffusivity of the mixture of TOPO and Alamine 336 is very close to the D in system with Alamine 336 alone. The values of the D estimated for individual reagents and their mixture are in complete agreement with that assumption. The estimated values of D for the mixture TOPO/Alamine 336 are of the same order of magnitude as the values of D for Alamine 336. In the case of mixture TOPO/LIX54 the average values of D for the mixture was estimated in relation to the appropriate values of D for the individual extractants. Moreover the magnitude of D is affected by the concentration of the compound.

Table 4. Values of diffusion coefficient for TOPO, LIX 54, ALAMINE® 336 and their equimolar mixture in the toluene/water system

c, mol/dm ³	Diffusion coefficient D, cm ² /s				
	LIX54	Mixture TOPO/LIX 54	TOPO	Mixture TOPO/ ALAMINE® 336	ALAMINE® 336
10 ⁻⁵	1.61·10 ⁻⁸	2.82·10 ⁻⁶	4.45·10 ⁻⁶	1.16·10 ⁻⁷	8.88·10 ⁻⁷
10 ⁻⁴	5.16·10 ⁻⁹	3.86·10 ⁻⁸	4.01·10 ⁻⁷	2.58·10 ⁻⁹	3.36·10 ⁻⁹
10 ⁻³	4.75·10 ⁻¹¹	4.49·10 ⁻¹⁰	2.16·10 ⁻⁹	5.79·10 ⁻¹¹	9.58·10 ⁻¹¹

CONCLUSIONS

It was found that the extraction efficiency of the investigated extractants are changed in the following order: Alamine 336>TOPO> β -diketone. The addition of the second extractant to the extraction system decreases the extraction efficiency. Moreover, the results obtained in toluene are much higher in comparison to the extraction of iron(III) in systems with Exxsol D220/230 as organic diluent. The initial rate of Fe(III) extraction is affected significantly by the composition of the extraction system and the type of the organic diluent. The highest results are obtained for the system with Alamine 336 in toluene as the diluent. A good agreement between the experimental and the correlated values of the concentration of metal ions estimated by the proposed model of mass transfer in a Lewis cell was obtained.

It was shown that the estimated values of the surface mole fraction at the mixed monolayer obtained from the interfacial tension measurements can be well correlated with the extraction data under similar conditions.

The FT-IR spectra of the investigated systems indicated that the extractants do not interact with each other. Probably the effect of the decreasing extraction efficiency could be explained by the different structure of the adsorbed mixed monolayer with the lower presence of TOPO at the saturated interface, not by interaction between the reagents.

ACKNOWLEDGMENTS

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