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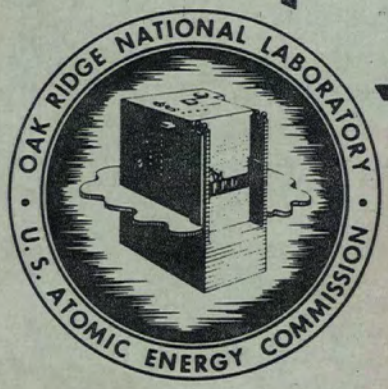
THE SOLVENT EXTRACTION OF IRON WITH TRI-N-OCTYLPHOSPHINE OXIDE

W. J. Ross
J. C. White



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W. J. Ross, J. C. White

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ABSTRACT

The extraction of iron from acidic solutions with tri-n-octylphosphine oxide (TOPO) was investigated. Iron is extracted only when the iron is in the trivalent oxidation state and sufficient chloride ion is present in solution. Quantitative extraction was observed when the solution was at least 4 M HCl or 1 M HCl-3 M NaCl. The loading capacity of 0.5 millimole of TOPO is approximately 16 mg of iron from 7 M HCl. Quantitative extraction of 12 mg of iron from 7 M HCl is possible in a single equilibration. Under these conditions extraction is quantitative at phase ratios as large as 20 to 1. The extracted species are probably $FeCl_3$ and $HFeCl_4$.

THE SOLVENT EXTRACTION OF IRON WITH TRI-N-OCTYLPHOSPHINE OXIDE

W. J. Ross, J. C. White

INTRODUCTION

In a previous report[7] the authors discussed the extraction of chromium from acidic solutions with tri-n-octylphosphine oxide (TOPO). This report, the extraction of iron with TOPO, is the second in a series of reports dealing with the extraction of various metal ions with alkyl phosphine oxides.

Brown and his coworkers,[1] in their original investigation on the extraction characteristics of uranium by alkyl phosphine oxides, found that the extraction coefficient of iron in 0.5 M solutions of chloride, at a pH of 1, was 0.4 as compared to 260 for uranium. In sulfate and nitrate solutions the extraction of iron was essentially non-existent. White and coworkers[6] reported that iron in the trivalent state was extracted from strong hydrochloric acid solutions by TOPO; however, they found little or no extraction in other acidic media. They also observed that ferrous iron was not extracted from chloride solutions, which indicated the possibility of a simple, straightforward separation of the two common oxidation states by solvent extraction.

In this investigation the solvent extraction behavior of iron has been more thoroughly examined and the effects of certain parameters on the extraction of iron have been noted.

REAGENTS

Ferric nitrate solution. Dissolve 36.2 grams of reagent grade $Fe(NO_3)_3 \cdot 9H_2O$ in 500 ml of one per cent HNO_3 to prepare a solution that contains approximately 10 mg of iron(III) per ml. Standardize the solution versus

potassium dichromate after reducing the iron(III) to iron(II) with stannous chloride and mercuric chloride.

Ferrous ammonium sulfate solution. Dissolve 35.1 grams of reagent grade $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in 500 ml of one per cent H_2SO_4 to prepare a solution that contains approximately 10 mg of iron(II) per ml. Standardize against potassium dichromate. Add an excess of stannous chloride solution before use.

Tri-n-octylphosphine oxide (TOPO), 0.1 M solution. Dissolve 38.6 grams of TOPO (> 99 per cent purity) in one liter of cyclohexane.

PROCEDURE

All extractions that involved the use of less than 20 ml of liquid were performed in the glass containers that have been described in an earlier paper.(7) When larger volumes of liquid were required, separatory funnels of various capacities were utilized.

Each test mixture was prepared by transferring the desired amount of standard iron(III) solution (10.4 mg of iron per ml) or iron(II) solution (10.2 mg of iron per ml) to the extraction vessel and then adding sufficient acid to form an aqueous solution of a predetermined concentration of the acid. In most tests the volume of the aqueous solution was five ml. Five ml of 0.1 M TOPO in cyclohexane was next transferred to the extraction vessel, after which the mixture was agitated on a Kahn shaker for the desired period of time.

After the equilibration period was over, the containers were allowed to stand in a specially designed rack until the phases separated completely and the mixture was clear. Test portions of the organic phase were removed by pipets, the organic diluent evaporated, and the TOPO decomposed with HNO_3 and

$HClO_4$ to form a residual solid that was dissolved in five per cent v/v H_2SO_4. The iron in this solution, as well as the iron in test portions of the aqueous phase of the mixture, was determined colorimetrically.(3) Specially designed absorption cells(4) were used in some cases to provide adequate sensitivity.

The extraction coefficient, E_a^o, was calculated from the concentrations of iron in the two phases after extraction and is defined as

$$E_a^o = \frac{\text{concentration of iron in organic phase}}{\text{concentration of iron in aqueous phase.}}$$

EXTRACTION OF IRON FROM CHLORIDE SOLUTIONS

Effect of Concentration of Hydrochloric Acid

The results of the extraction of iron from chloride systems with TOPO at various concentrations of hydrochloric acid are shown in Table I and Figure 1.

Table I

Extraction of Iron from Hydrochloric Acid Solutions with TOPO
Effect of Acid Concentration

Iron(III) - 8.16 mg
Iron(II) - 10.2 mg
TOPO - 5 ml 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio - 1

	HCl, Molarity	Iron, mg Organic	Iron, mg Aqueous	E_a^o
Iron(III)	1	3.23	4.93	0.65
	4	7.79	0.372	21.0
	7	8.15	0.009	906
	10	8.16	0.002	4080
Iron(II)	1	0.1	10.1	0.01
	4	0.2	10.0	0.02
	7	0.1	10.1	0.01
	10	0.2	10.0	0.02

In chloride media, iron is extracted only when present in the trivalent state. Ferrous iron is not extracted under the conditions of the tests

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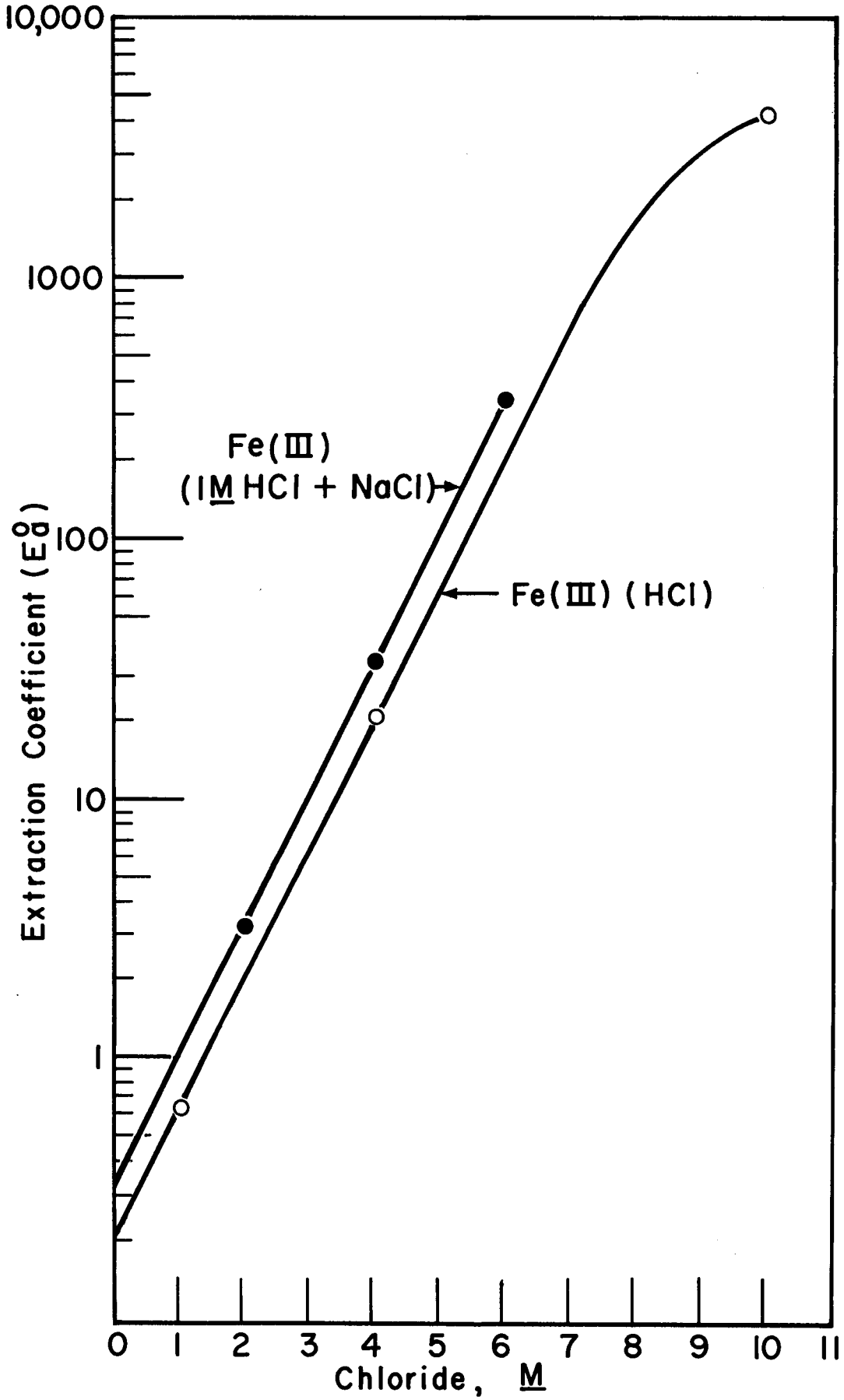

FIG. 1, Extraction of Iron from chloride solutions with Tri-n-octylphosphine oxide

thereby providing an obvious means for separating the two oxidation states of iron. The degree of extraction is markedly affected by the concentration of hydrochloric acid present in the solution. The extraction coefficient varies from 0.6 in 1 M HCl to 4000 in 10 M HCl. This effect is similar in nature to that found when iron is extracted with ethers from acidic chloride systems. With ethers the extraction coefficient is also increased tremendously by increasing the concentration of HCl in the extraction medium.

Effect of Chloride Concentration

A series of extractions of iron was made from solutions in which the concentration of the hydrogen ion was held constant at one molar and the concentration of chloride ion varied from one to seven molar by the addition of sodium chloride. The results are shown in Table II and Figure 1.

Table II

Extraction of Iron from Chloride Solutions
Effect of Concentration of Chloride

Iron(III) - 8.16 mg
TOPO - 5 ml 0.1 M in cyclohexane
HCl - 1 M
Equilibration time - 10 minutes
Phase ratio - 1

NaCl, M	Iron, mg		E_a^o
	Organic	Aqueous	
1	6.14	2.02	3.03
3	7.93	0.231	34.3
5	8.13	0.025	331
6*	8.14	0.022	377

* Saturated solution.

The results are similar to those obtained in the tests where the hydrochloric acid concentration was varied in that the extraction coefficient

increased with increasing concentration of sodium chloride. On the basis of these experiments the extraction of iron from chloride systems is obviously a function of the concentration of the chloride ion per se and not acidity, although high hydrogen ion concentrations do not vitiate the extraction. For most analytical applications the lowest permissible acid concentration is usually preferred. On this basis, a solution 1 M HCl and 5 M NaCl is an ideal medium for the extraction of iron with TOPO.

Effect of Concentration of Iron

The degree to which various amounts of iron were extracted from 7 M HCl by five ml of 0.1 M TOPO is presented in Table III and Figure 2.

Table III

Extraction of Iron from Chloride Solutions
Effect of Concentration of Iron

HCl - 7 M
TOPO - 5 ml 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio - 1

Iron, mg			
Taken	Found		E_a^o
	Organic	Aqueous	
4.2	4.2	0.0	> 1000
7.14	7.14	0.005	1590
8.16	8.15	0.009	948
9.18	9.17	0.014	646
10.2	10.2	0.036	283
12.2	12.1	0.075	161
13.3	13.1	0.225	58
14.3	13.7	0.640	21
15.3	13.9	1.38	10
18.7	15.0	3.73	4
20.8	15.5	5.30	3
50.6	15.6	35.0	0.4
101.1	15.8	85.3	0.2

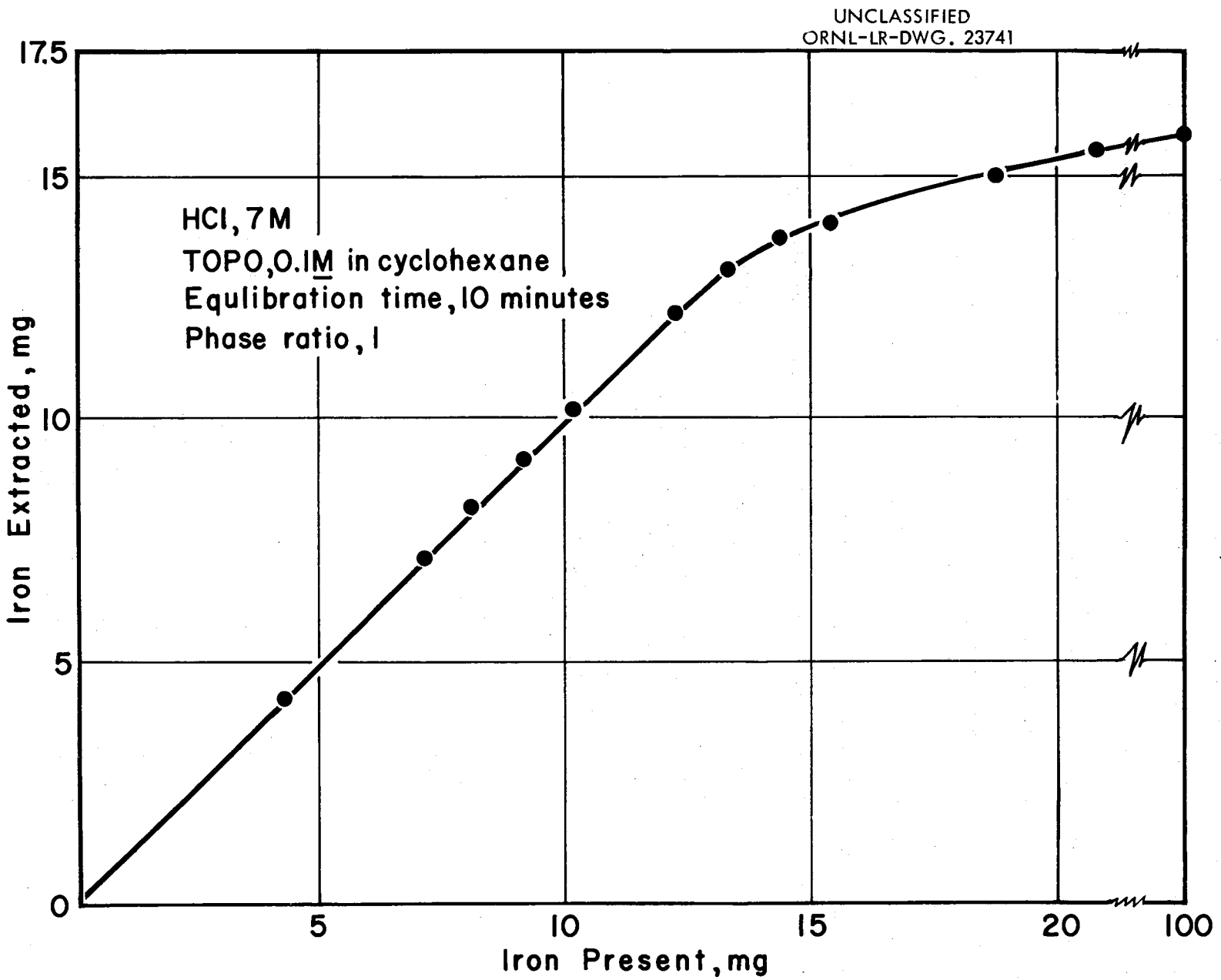

FIGURE 2, Extraction of Iron III from Chloride Solutions with Tri-n-octylphosphine oxide

The extraction of 12 mg of Fe^{+3} is more than 99 per cent complete after a single equilibration. Deviation from quantitative extraction becomes increasingly larger as the saturation value of the reagent is approached. This value, approximately 16 mg of Fe^{+3} per 0.5 millimoles of TOPO, corresponds to a molar ratio, $C_{TOPO}/C_{Fe^{+3}}$, of two.

Effect of Concentration of Tri-n-octylphosphine Oxide

The stoichiometric relationship between iron and TOPO in the organic phase was investigated by varying the concentration of TOPO in systems that contained an excess of iron. The results are presented in Table IV.

Table IV

Extraction of Iron from Chloride Solutions
Effect of Concentration of
Tri-n-octylphosphine Oxide

Iron(III) - 41.6 mg
Equilibration time - 10 minutes
Phase ratio, O/A - 5/7

HCl, M	TOPO, M	Iron, mg		C_{TOPO}/C_{Fe}
		Organic	Aqueous	
7	0.01	4.6	37.0	0.6
	.05	6.7	34.9	2.1
	.10	14.2	27.4	2.0
	.15	21.7	19.9	1.9
	.20	29.8	11.8	1.9
1	0.01	11.6	30.0	0.2
	.05	13.2	28.4	1.0
	.10	15.5	26.1	1.8
	.15	19.1	22.5	2.2
	20	23.5	18.1	2.4

The data that were obtained in 7 M HCl systems reveal that a continuous enhancement of iron occurs in the organic phase as the concentration of TOPO is increased. In all systems, except that in which the concentration of TOPO

is 0.01 M, the combining ratio between TOPO and iron, in the organic phase, is approximately two. When the amount of iron present is in very large excess over the loading value of TOPO, e.g. in 0.01 M TOPO systems, the combining ratio is considerably lower.

The combining ratios that are obtained in 1 M HCl systems increase as the concentration of TOPO is increased. This continuous increase is indicative of a different extraction mechanism in 1 M HCl systems than in 7 M HCl wherein the degree to which iron is extracted is dependent on the concentration of the extractable species of iron in the aqueous solution as well as on the concentration of TOPO.

Effect of Time on Extraction of Iron

The effect of equilibration time on the extraction of iron from chloride solutions is shown in Table V.

Table V

Extraction of Iron from Acid Solutions
Effect of Extraction Time

Iron(III) - 20.8 mg
TOPO - 0.1 M in cyclohexane
HCl - 7 M
Phase ratio, organic/aqueous - 1

Time, Minutes	Iron, mg	
	Organic	Aqueous
10	15.7	5.1
15	15.5	5.3
60	15.8	5.0

Inasmuch as the results are essentially identical, an equilibration time of 10 minutes is sufficient for such an extraction.

Effect of Phase Ratio

In all previous tests the volumes of the aqueous and organic phases were equal. In order to determine if this ratio affected the extraction of iron and, similarly, to determine if larger aqueous volumes could be tolerated, a series of extractions was performed on systems of constant volume of organic reagent and variable aqueous volumes. The amount of iron in the original aqueous solution was adjusted so that the effect of the volume ratio could be determined under conditions in which quantitative extraction occurs, as well as those where excess iron was present when the ratio is unity. The results of these tests are given in Table VI.

Table VI

Effect of Phase Volume Ratio on the Extraction of Iron from Chloride Solutions

HCl - 7 M
TOPO - 5 ml of 0.1 M in cyclohexane
Equilibration time - 10 minutes

V_a/V_o	Iron, mg			E_a^o	Per Cent Extracted
	Taken	Found			
		Organic	Aqueous		
1	10.2	10.2	0.036	283	99
5		10.2	0.007	7030	99
10		10.2	0.017	6180	99
20		10.2	0.018	11300	99
1	12.5	12.2	0.313	39	98
2		12.4	0.055	450	99
3		12.4	0.060	620	99
1	14.6	13.1	1.45	9	90
2		14.0	0.61	46	96
3		13.9	0.72	57	95
1	20.8	15.5	5.3	3	75
5		14.0	6.8	10	67
10		14.0	6.8	21	67
20		14.2	6.6	43	68

As much as 12.5 mg of iron is quantitatively extracted by 0.5 millimoles of TOPO at aqueous to organic phase ratios of as large as 20. Extremely large extraction coefficients are obtained which increase with increasing phase ratio. When the loading capacity of the TOPO is exceeded, however, for example in the case of 20.8 mg of iron, the extraction coefficient is not materially increased by large phase ratios. It is obvious from these results that efficient separation or concentration of significant amounts of iron from relatively large aqueous volumes is readily achieved by the use of TOPO.

Identification of Extracted Species

In an effort to identify the species in which iron existed in the organic extract, experiments were conducted in which various amounts of iron were extracted from solutions of varying concentration of chloride and hydrogen ions. The chloride to iron and TOPO to iron ratios were calculated by determining the concentrations of chloride, iron and TOPO in the organic extract. Chloride was determined by direct titration with silver nitrate or by stripping the organic phase with 0.15 M H_2SO_4 and then titrating the acidic solution with silver nitrate. Iron was determined potentiometrically in the sulfuric acid strip solution by titration with a standard solution of potassium dichromate. Since TOPO is not soluble in acidic solutions, the concentration of TOPO in the organic extract was assumed to be the same as that originally taken, 0.5 millimoles. The results are shown in Table VII.

Table VII

Composition of Organic Extract after Extraction of Iron from Chloride Solutions with Tri-n-octylphosphine Oxide

TOPO - 5 ml, 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio - 1

HCl Molarity	NaCl Molarity	Chloride	Iron, Taken mg	Chloride/ Iron	TOPO/ Iron
1	-	1	184	2.9	1.6
			92	3.0	2.0
			48	3.0	2.4
			23	3.1	3.3
3	-	3	184	3.2	1.6
			92	3.3	1.7
			48	3.4	1.8
			23	3.5	2.0
5	-	5	184	3.2	1.5
			92	3.2	1.6
			48	3.3	1.7
			23	3.5	1.8
7	-	7	184	3.3	1.4
			92	3.2	1.5
			48	3.5	1.7
			23	3.5	1.7
1	1	2	184	3.0	1.5
			92	3.0	1.6
			48	2.9	1.9
			23	3.1	2.3
1	2	3	184	3.0	1.5
			92	3.0	1.6
			48	3.0	1.8
			23	3.1	2.0
1	4	5	184	3.1	1.4
			92	3.1	1.5
			48	3.1	1.6
			23	3.3	1.8
1	6*	7*	184	3.0	1.4
			92	3.3	1.6
			48	3.1	1.6
			23	3.2	1.8

* Saturated

The chloride to iron ratio is three, in 1 M HCl, which indicates that $FeCl_3$ is the extracted species. As the HCl concentration is increased, the ratio increases to a maximum of 3.5. A possible explanation of this increase is that iron is also extracted as $HFeCl_4$. In strong hydrochloric acid media, iron is known to exist[3] in both forms, $FeCl_3$ and $HFeCl_4$. Since the extraction of iron is definitely enhanced by the addition of hydrochloric acid, it would appear that iron is extractable by TOPO as either $FeCl_3$ or $HFeCl_4$. In less concentrated hydrochloric acid solutions, iron exists to some degree as FeCl and $FeCl_2$ which apparently are not extracted by TOPO. A detailed study of the extraction mechanism as correlated with absorption spectra of the organic solutions will be discussed completely in another paper.[2]

The TOPO to iron ratio in hydrochloric acid media is fairly constant at about 1.7 except in 1 M HCl where the ratio is dependent on the concentration of iron concerned.

In HCl-NaCl solutions, where the hydrogen ion concentration is held constant at 1 M and the chloride ion concentration increased by addition of sodium chloride, the chloride to iron ratio is essentially constant at three. The TOPO to iron ratio, as in HCl solutions, varies with the iron concentration originally present. Clarification of the mechanics of extraction from HCl-NaCl solutions will also be reported in a separate paper.[2]

Extraction of Iron from Other Acid Systems

The extraction of iron from sulfuric, nitric, perchloric, and phosphoric acid systems with tri-n-octylphosphine oxide was determined as previously described. The results are shown in Table VIII.

Table VIII

Extraction of Iron with TOPO from Sulfuric, Nitric, Phosphoric and Perchloric Acid Solutions
Effect of Acid Concentration

Iron(III) - 10.4 mg
Iron(II) - 10.2 mg
TOPO - 5 ml 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio - 1

Iron Oxidation State	Acid		Iron, mg		E_a^o
	Type	Molarity	Organic	Aqueous	
+3	H_2SO_4	1	< 0.1	10.4	< 0.01
		4	< .1	10.4	< .01
		7	< .1	10.4	< .01
		10	.5	9.9	.05
	HNO_3	1	0.2	10.2	0.02
		4	.1	10.3	.01
		7	< .1	10.4	< .01
		10	.9	9.5	.09
	H_3PO_4	1	0.1	10.3	0.01
		4	< .1	10.4	< .01
		7	.6	9.8	.06
		10	< .1	10.4	< .01
	$HClO_4$	1	< 0.1	10.4	< 0.01
		4	< .1	10.4	< .01
		7	< .1	10.4	< .01
		10	< .1	10.4	< .01
+2	H_2SO_4	1	< 0.1	10.1	< 0.01
		4	< .1	10.3	< .01
	HNO_3	1	< 0.1	10.3	< 0.01
		4	< .1	10.5	< .01
	H_3PO_4	1	< 0.1	10.2	< 0.01
		4	< .1	10.3	< .01
	$HClO_4$	1	< 0.1	10.5	< 0.01
		4	< .1	10.5	< .01

It is obvious that iron is not extracted from any of the systems that were tested. These results are further confirmation that iron is extracted in the form of a ferric chloride complex and point out the utilitarian value of tri-n-octylphosphine oxide as a reagent for the separation of iron.

Effect of the Addition of Chloride on the Extraction of Iron from Nitric or Sulfuric Acid Solutions

Inasmuch as nitric and sulfuric acids are commonly used in the dissolution of various types of materials that contain iron, tests were conducted to determine the effect of added chloride ion on the applicability of TOPO as an extractant for iron from these solutions. The chloride was added either as sodium chloride or hydrochloric acid. The results are shown in Table IX.

Table IX

Effect of Chloride on the Extraction of Iron from Nitrate and Sulfate Solutions with TOPO

Iron(III) - 5 ml, 10.4 mg
TOPO - 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio, aqueous/organic - 1

Concentration of Solution, Molarity				Iron, mg		E_a^o
HNO_3	H_2SO_4	HCl	NaCl	Organic	Aqueous	
1	-	7	-	9.6	0.8	12
3	-	7	-	9.6	0.8	12
1	-	-	~3	7.6	2.8	2.7
3	-	-	~3	5.8	4.6	1.3
-	1	7	-	10.4	0.02	520
-	3	7	-	10.3	0.10	103
-	1	-	~3	9.1	1.3	7.0
-	3	-	~3	10.4	0.05	208

The results show that the addition of chloride, either as sodium chloride or hydrochloric acid, to 1 or 3 M nitric or sulfuric acid, beneficiates the

extraction of iron markedly. In a solution, 3 M H_2SO_4 and 7 M HCl, the extraction coefficient is essentially identical to that in a 7 M solution of HCl with no sulfuric acid present. Sodium chloride is equally effective only when the hydrogen ion concentration is around three molar. The extraction coefficient increased tremendously when the acid concentration was increased from one to three molar in the presence of 3 M NaCl.

Beneficiation of the extraction coefficient is not nearly as marked in the nitrate media as in the sulfuric systems. Whereas the extraction of iron from sulfate solution is made quantitative in a single equilibration by the addition of chloride, the extraction from nitrate solution under identical chloride concentrations is only 90 per cent complete. Several equilibrations would be required to extract iron quantitatively.

Hydrochloric acid, 7 M, apparently increases the extraction of iron more than sodium chloride from nitrate solutions.

Effect of Solvent

In previous papers concerning the extraction of uranium and chromium with TOPO it was shown that the extraction of uranium was greater in such slightly polar solvents as cyclohexane or kerosene than in more polar systems such as alcohols, but that the polarity of the solvent was not an important factor in the extraction of chromium.

A similar investigation of the effect of the solvent on the extraction of iron was performed with solutions of TOPO in the various solvents that are listed in Table X. The results are very similar to those that were obtained in the extraction of chromium in that the extraction coefficients that were obtained with non-polar solvents (cyclohexane, Varsol, and carbon

tetrachloride) were approximately the same and about four times less than the coefficient that was obtained with more polar solvents as nitrobenzene. The extraction of iron is, therefore, enhanced to some extent by the use of more polar solvents. Nitrobenzene, however, is undesirable as a solvent for TOPO in the extraction of iron inasmuch as the yellow color of the solvent would interfere with any subsequent determinations of iron through spectrophotometric measurements of the color of the organic phase. The significantly lower extraction coefficient that was obtained with TOPO in capryl alcohol indicates that such relatively viscous solvents are unacceptable.

Table X

Extraction of Iron from Chloride Solutions
Effect of Solvent

TOPO - 0.1 M
HCl - 4 M
Iron - 8.2 mg
Phase ratio - 1
Equilibration time - 10 minutes

Solvent	Dielectric Constant at 25° C.	E_a^o
Cyclohexane	2.015	49
Carbon tetrachloride	2.298	39
Varsol	-	35
Capryl alcohol	-	5
Nitrobenzene	34.82	170

SUMMARY

Iron is extracted quantitatively by TOPO only when in the trivalent oxidation state in a chloride medium. No extraction occurs in other media. Divalent iron is not extracted under any conditions tested.

The extraction of iron is a function of the chloride concentration. In hydrochloric acid solutions, the extraction coefficient for iron increases from 0.65 in 1 M HCl to greater than 4000 in 7 M HCl. When the HCl concentration is held constant at one molar, the addition of chloride as sodium chloride results in increased extraction of iron. For example, in a solution 1 M HCl, 5 M NaCl, the extraction coefficient of iron is greater than 300. Although the extraction of iron from solutions other than those which contain chloride is essentially nil, the addition of chloride to sulfate, nitrate, etc. solutions results in the extraction of iron. The extraction is quantitative if sufficient chloride is added.

The loading capacity of 0.5 millimoles of TOPO is approximately 16 mg of iron from 7 M HCl. Quantitative extraction of 12 mg of iron from 7 M HCl is possible in a single equilibration.

The molar combining ratio of TOPO to iron is two for a range of 0.05 to 0.2 M TOPO.

Equilibration is reached rapidly. No significant difference in the extraction coefficient was noted between 10 and 60 minutes.

Greater than 99 per cent of the iron is extracted from 7 M HCl at aqueous to organic phase ratios as large as 20 to one.

The composition of the extracted species is not precisely known but probably consists of a mixture of $FeCl_3$ and $HFeCl_4$. The chloride to iron

gram atom ratio is three in 1 M HCl and in HCl-NaCl solutions. The ratio is slightly higher in more concentrated hydrochloric acid solutions.

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