공학석사학위논문

A Study on metal removal in crude oil using low−molecular−mass organic acids

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A Study on metal removal in crude oil using low-molecular-mass organic acids

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Abstract

Crude oil contains several metal contaminants such as iron, vanadium and nickel, and these trace metals have deleterious effect on oil refinery. For example, they can contribute to corrosion of plant unit, heat exchanger fouling. Among the problematic situations caused by metals in crude oil, catalyst deactivation is of major concern in oil refinery. In other words, metals such as vanadium, nickel and iron can cover the surface of the catalysts and disturb their normal activity. Because of these reasons, the demand for demetallization in crude oil has been increased for the past few decades.

Some part of metals in crude oil can be removed by electric desalter, when they exist as form of inorganic salts such as inorganic oxides or sulfides. However, large portions of metals are usually in the form of organometallic complexes, which are difficult to be removed in desalting process because of their oleophilic characteristic and poor solubility in water.

Iron can also exist as a complex form with various organic compounds, such as a form of iron carboxylate. We used iron standard solution (1,000 μg/g, in 75 cSt hydrocarbon oil), iron (III) 2-ethylhexanoate and iron (III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate) as model compounds. These model compounds were reacted with

aqueous solution of several organic acids. As a result, organic acids such as citric acid and ethylenediaminetetraacetic acid (EDTA) disodium salt shows remarkable effect in removal of iron from model compounds. Maleic acid was also effective for removal of iron showing positive results.

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conc.   concentrated

EDTA   ethylenediaminetetraacetic acid

eq.   equivalent

g   gram(s)

mg   milligram(s)

μg   microgram(s)

mL   milliliter(s)

cSt   centistoke(s)

h   hour(s)

ICP   inductively coupled plasma

AES   atomic emission spectroscopy

mM   mmole(s)/liter

mmol   millimole(s)

ppm   parts per million

LPG   liquefied petroleum gas

Fe-EH   iron (III) 2-ethylhexanoate

Fe(TMHD)$_3$ iron (III) tris (2,2,6,6-tetramethyl-3,5-heptane

                dionate)

rpm   revolution per minute

Introduction

1.1. Problematic activities of trace metals in crude oil

Crude oil introduced to oil refinery process contains a lot of undesirable impurities such as nonmetallic or metallic impurities. In the case of nonmetallic impurities, it includes sulfur, oxygen, nitrogen, etc. In the case of metallic impurities, trace metals such as vanadium, nickel and iron are known to be exist in crude oils.

The trace metals not only contaminate the products, but also have deleterious effect on the oil refinery plant unit. For example, they can produce dry-sludge and cokes which preclude flow of the fuel oil and cause maldistribution inside the plant unit. And in the case of inorganic salts, they can be deposited in the heaters and pre-heat exchangers producing hydrogen chloride gas. This gas condenses to hydrochloric acid and it causes serious corrosion of plant equipment. And also, inorganic salts such as iron sulfide and oxide can precipitate each other causing plugging problem in oil refinery plants. Because of these detrimental activities of trace metals, they are known to be of major concern in oil refinery and should be removed.

After all, it is the major problem that these kind of metals can have a

deleterious effect on the catalysts used in oil refinery process. For example, metals such as vanadium, nickel and iron can cover the surface of the catalysts and disturb their normal activity. What is worse, some metals can destroy the structure of the catalysts causing catalytic inactivity and the fragments of destroyed catalysts produce gas and cokes which have bad influence on the other crucial products. Because of these poisoning effects, the demand for removal of trace metals in crude oil has been increased for the past few decades.

Metals in crude oil can exist as several forms. For example, some of the metallic contaminants are present as inorganic salts, such as inorganic oxides, sulfides, etc. These kind of metallic compounds can be easily removed by water-washing during the desalting process. However, large portions of metals are usually in the form of organometallic complexes. They are sometimes thermally stable and have poor solubility which made the removal of vanadium and nickel in desalting process difficult. Iron can also exist as a complex form with various organic compounds and they are hardly removed in the desalting process because of their oleophilic characteristic and poor solubility in water.

Only a small portion of remaining metals whose size is under $25\,\mu$m can be removed by filtration in the post process. In other words, large

amount of metals would not be removed and concentrated in the residual crude oil. They can cause pore clogging, slagging and fouling and also reduction of catalytic activity by covering up the catalysts' surface. In this way, metals shorten the period of usage of catalysts and lead to uneconomical situation

Therefore, trace metals in crude oil should be removed. There is a need about new method for removing metals from crude oil. By removing a lot of metal components in the crude oil, we can achieve a dramatic reduction of the costs for purchasing new catalysts and increase the productivity in oil refinery system.

1.2. Desalting process for removal of metals in crude oil

One of the common processes for removal of metal contaminants is electric desalting process, usually the first process in oil refinery. First, crude oil and water are rigorously mixed through the pipe line. In this process, metallic contaminants which are present as inorganic salts can be dissolved in aqueous phase. And next, this mixture enters into the electric desalter where a voltage is applied to increase the surface area of water droplets. And then, water droplets aggregate each other and the larger drops can sink down to the bottom of the desalting unit. In this way, electric desalter leads to coalescence of water molecules and separation of oil and aqueous phase, and the separated aqueous phase is removed.

However, only inorganic salts such as sodium chloride or magnesium chloride can be removed by this process. Organometallic compounds such as metalloporphyrin or other organometallic complexes, are not readily removed by this electric desalter because of their poor solubility in water. So large portion of metals are hardly removed in this unit and remain in the crude oil causing many problematic situations.

So we designed a new method for removal of metal contaminants by

adding demetallizing agent before the desalting process. Demetallizing agent should be dissolved in the aqueous phase and react with organometallic complex giving free metal ions. For example, metal chelating agent which have greater metal−bonding energy can be used. This agent will chelate metal ions and dissolved into water phase, and this water phase will be removed out. Also, acids can be used in this process. Acids can produce H+ ion and this can react with organometallic complex giving metal free complex and metal−carboxylate. This metal carboxylate can be easily dissolved into water phase, removing metals from crude oil. There are a lot of patents about removal of metals by using inorganic acids. [1] For example, there were efforts for removal of metals using sulfuric acid [2], but sulfuric acid may produce sludge causing emulsion in oil refinery. And inorganic acids can also corrode the plant and can have bad influence on the process unit. [3] In the case of organic acids, they are relatively less harmful to the process. And because of their moderate prices, organic acid can be used for demetallizing agent in the oil refinery.
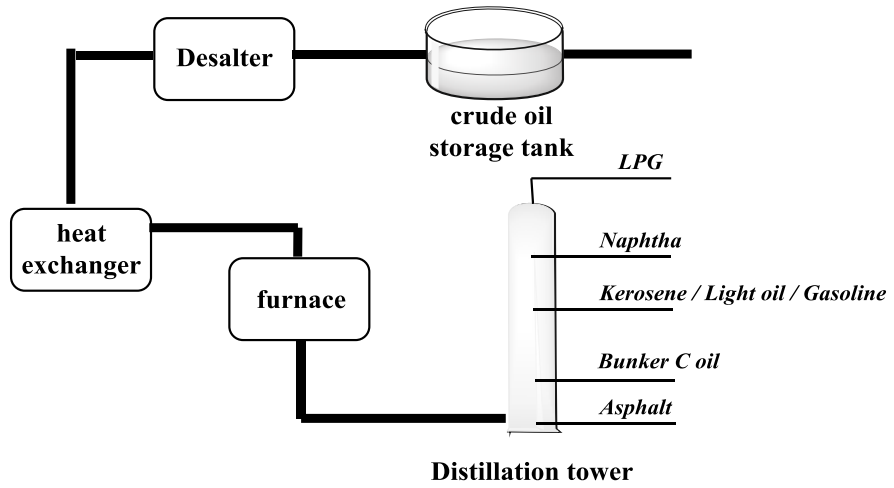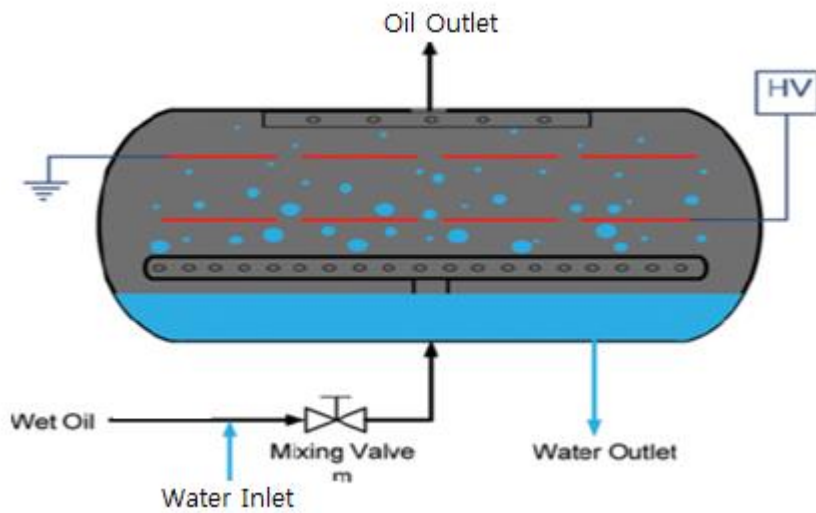
Figure 1. Conventional oil refinery

Figure 2. Cross-sectional diagram of electric desalter

1.3. Iron in crude oil

In common with other heavy meals in crude oils, iron can contribute to corrosion of plant unit, heat exchanger fouling, furnace coking and product degradation in refining and other process. Among the problematic situations caused by metal contaminants in crude oil, catalyst deactivation is of major concern in oil refinery. For example, iron can react with hydrogen sulfide in crude oil and this produces iron sulfide [4], which covers the surface of the catalysts leading to catalytic deactivation. The reaction can be represented as below.

$$Fe(RCOO)_2 + H_2S + 6H_2 \longrightarrow FeS + 2RCH_3 + 4H_2O$$
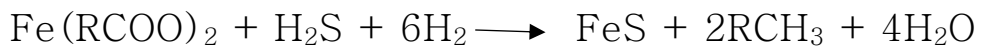
Because of this catalytic deactivation during the catalytic cracking, there can be a loss of conversion ratio.

There are several methods to remove iron from crude oil. For example, magnetic separation technology is used to separate iron from crude oil by using the magnetic separator, however, only about 40% of iron can be removed by this process, averagely. Iron adsorption technology can be also used for removal of iron in crude oil. Iron adsorption technology uses sulfur in a fiber to react with iron producing iron sulfide deposits on the fiber, and the produced iron sulfide then accelerated the reaction

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between iron and sulfur. However, this technique needs a long-term operation, which is industrially difficult, and also the unreacted iron still exist.

Because of these reasons, there is a need for removal of iron in crude oil. In general, electric desalting process is used for deferrization but the majority or the iron is not removed and remains in residual crude oil. So in this paper, we use several aqueous solution of chemical reagents to react with organic iron compounds and extract the iron ion into aqueous phase. This is a very effective and simple technique, because there is no need for purchasing additional instrument in oil refinery. In this paper, we used several iron model compounds to test the possibility about removal of iron.

1. General procedures

We conducted experiment with model compounds to test the removal efficiency of iron when using several organic acids. We made organic solution of model compound and mixed with aqueous solution of organic acids. After reaction, we separated organic phase and aqueous phase by separatory funnel. Analysis was conducted by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

organic solution of model
compound or crude oil
+
aqueous solution of reagent

80 $^\circ$C, 5 h

1500 rpm

Two phase was separated
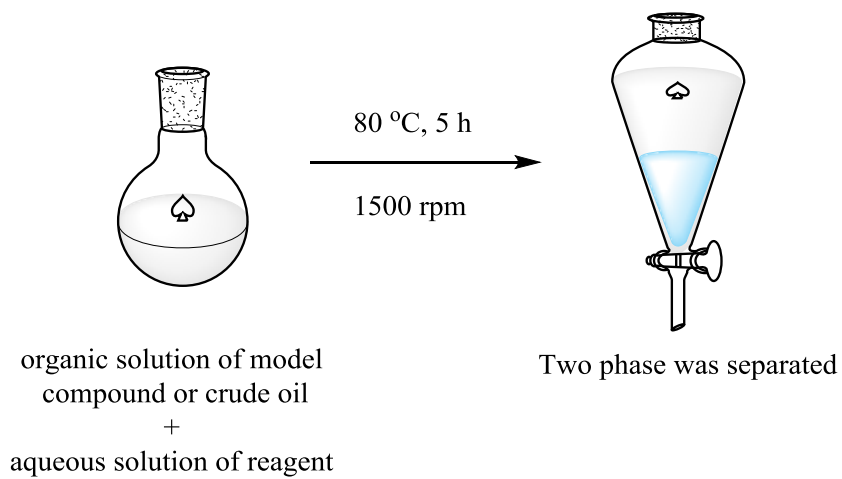
Scheme 1. Strategy for experiment of model compound or crude oil with
demetallizing reagents.

2.1 Removal of iron

　Iron contents in crude oil have bad influence on oil refinery and the major problem is a loss of catalytic activity. Iron elements in crude oil usually are in the form of inorganic salts or organometallic complexes, and the former is easily removed by electric desalting equipment but the latter is not. When metals are chelated in organic materials, it is more harmful in catalytic inactivation and more difficult to be removed because of their poor solubility in water. [5] So, in this paper, we investigated a proper method for removal of iron chelated in organic materials by using model compounds and four different crude oils.

First, we used iron standard solution (1,000 μg/g, in 75 cSt hydrocarbon oil). Iron standard solution is a material used in Inductively Coupled Plasma−Atomic Emission Spectroscopy (ICP−AES) analysis, and it consist of mineral oil which is derived from crude oil. The major component of mineral oil is hydrocarbon, and the exact component is not known. We made 10 ppm solution of iron standard solution by diluting original 1000 ppm solution using xylene..

We also used iron (III) 2−ethylhexanoate and iron (III) tris(2,2,6,6−tetramethyl−3,5−heptanedionate) as model compounds. Both iron (III)

2-ethylhexanoate and iron (III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate) are soluble in several organic solvents such as methylene chloride, toluene and xylene, and we chose xylene as a solvent. In common with iron standard solution, we made 10 ppm solution of iron (III) 2-ethylhexanoate and iron (III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate).

Next, we choose reagents to remove metal ions from iron standard solution, iron (III) 2-ethylhexanoate and iron (III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate) . We used organic acids such as maleic acid, citric acid and EDTA disodium salt, formic acid, glutaric acid, fumaric acid and succinic acid. We anticipated these organic acids could be effective for removal of metals from model compounds and crude oils.

2.1.1 Removal of iron from iron standard solution.

First, we conducted experiment with 10 ppm solution of iron standard in xylene with aqueous solution of organic acids. After vigorous mixing, the two phase was separated and the aqueous phase was analyzed by Inductively Coupled Plasma−Atomic Emission Spectroscopy (ICP−AES).

The iron concentration of starting solution in xylene was 9.27 ppm. Some results shows higher data than 9.27 ppm because of an instrumental error and the maximum error rate was about 7.3 %.

As you can see in the table, citric acid and EDTA disodium salt shows good results, in other words, almost all iron was removed. Maleic acid also shows good results showing 69 % of removal effeciency and other acids such as formic, fumaric, succinic and glutaric acid were not effective for removal of iron from this solution.

Reagents	Experiment	Iron concentration in aqueous phase (ppm)	Average (ppm)	Removal Percentage (%)
D.W	1	0.05	0.11	1.19
	2	0.14		
	3	0.14		
Maleic acid	1	6.32	6.40	69.04
	2	6.45		
	3	6.43		
Formic acid	1	0.38	0.42	4.53
	2	0.44		
	3	0.44		
EDTA disodium salt	1	9.15	9.44	101.83
	2	9.56		
	3	9.6		
Citric acid	1	10.41	10.43	112.51
	2	10.17		
	3	10.72		
Fumaric acid	1	0.52	0.45	4.85
	2	0.33		
	3	0.5		
Succinic acid	1	0.16	0.92	9.92
	2	1.54		
	3	1.05		
Glutaric acid	1	0.08	0.91	9.82
	2	2.36		
	3	0.29		

Table 1. The removal percentage (%) after reaction with iron standard solution
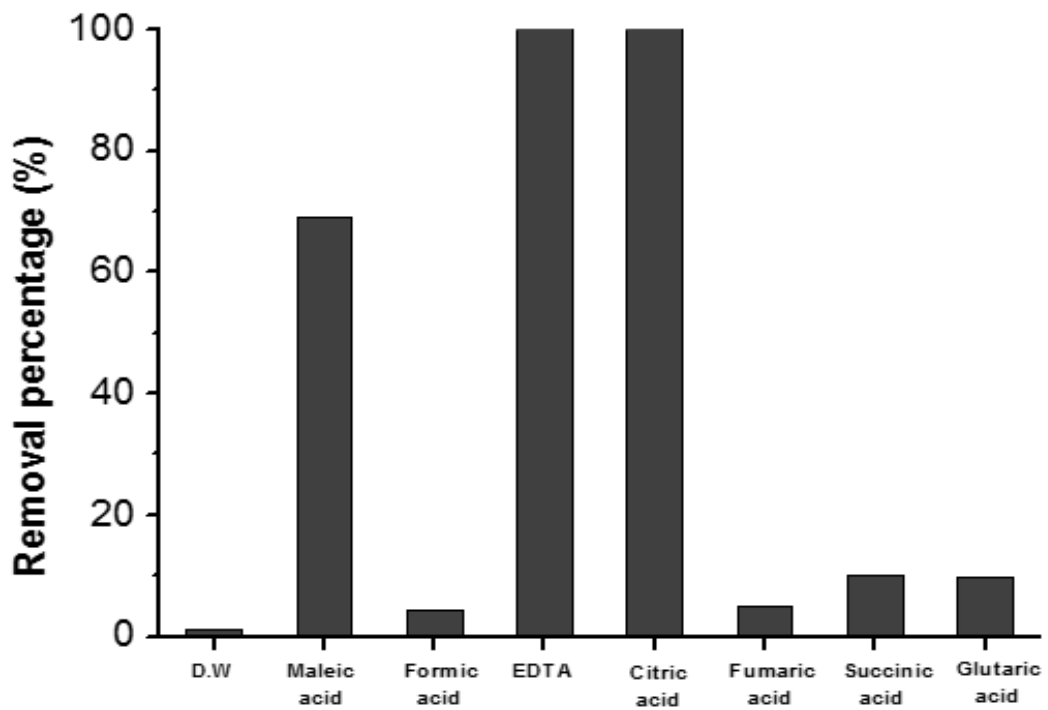
Figure 3. Removal percentage of iron from iron standard solution

2.1.2 Removal of iron from iron (III) 2-ethylhexanoate

Next, we reacted 10 ppm solution of iron (III) 2-ethylhexanoate (Fe-EH) in xylene with several aqueous solution of organic acids. After reaction, in common with the former case, the aqueous phase was separated and analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

The iron concentration of iron (III) 2-ethylhexanoate starting solution in xylene was 6.297 ppm. Some results shows higher data than 6.297 ppm because of an instrumental error and the maximum error rate was about 0.8%.

In common with the former case, EDTA disodium salt, citric acid and maleic acid show remarkable results, in other words, over 80% of iron was removed when using these kind of organic acids. Other organic acids such as formic, furamic, succinic and glutaric acid were not effective for removal of iron from this model compound.

Reagents	Experiment	Iron concentration in aqueous phase (ppm)	Average (ppm)	Removal Percentage (%)
D.W	1	0	0	0
	2	0		
	3	0		
Maleic acid	1	5.22	5.15	81.78
	2	5.12		
	3	5.11		
Formic acid	1	0.11	0.08	1.27
	2	0.06		
	3	0.07		
EDTA disodium salt	1	5.50	5.51	87.50
	2	5.87		
	3	5.17		
Citric acid	1	6.02	6.00	95.28
	2	6.35		
	3	5.64		
Fumaric acid	1	0.95	0.67	10.64
	2	0.66		
	3	0.41		
Succinic acid	1	0.04	0.14	2.22
	2	0.08		
	3	0.29		
Glutaric acid	1	0.01	0.08	1.27
	2	0.13		
	3	0.08		

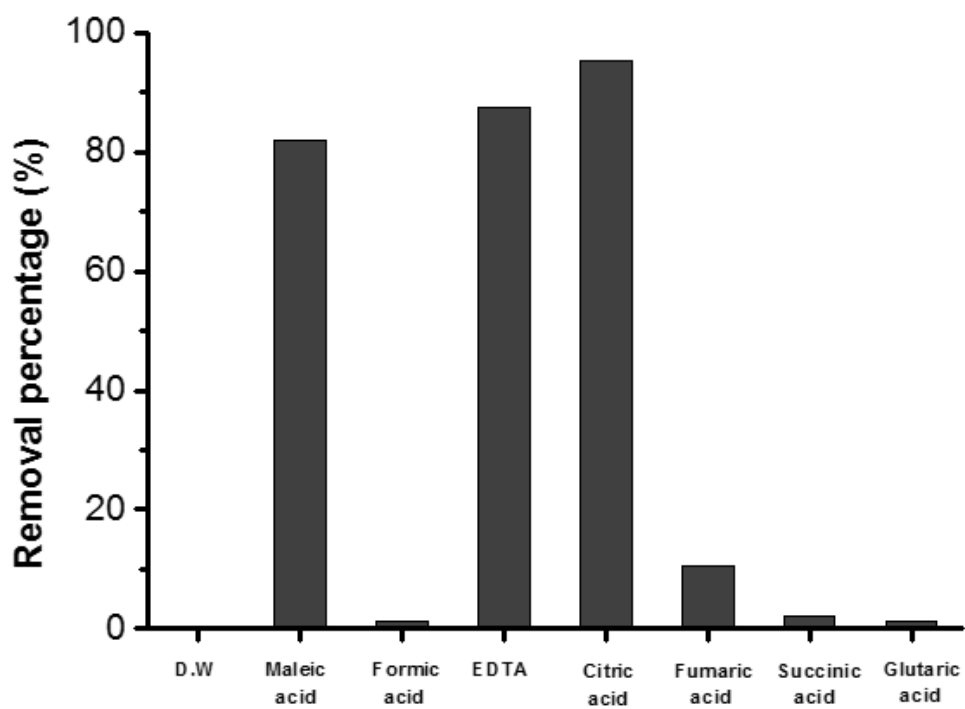Table 2. The removal percentage (%) after reaction with Fe-EH

Figure 4. Removal percentage of iron from iron (III) 2-ethylhexanoate

2.1.3 Removal of iron from iron (III) tris (2,2,6,6-tetramethyl-3,5-heptanedionate)

We also conducted reaction with iron (III) tris (2,2,6,6-tetramethyl-3,5-heptanedionate) (Fe(TMHD)$_3$) with several aqueous solution of organic acids. After reaction, the aqueous phase was separated and analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

The iron concentration of starting solution of iron (III) tris (2,2,6,6-tetramethyl-3,5-heptanedionate) in xylene was 10.08 ppm. Some results shows higher data than 10.08 ppm maybe because of an instrumental error.

In common with the former case, maleic acid, EDTA disodium salt and citric acid shows remarkable results, in other words, over 85% of iron was removed when using these kind of organic acids, averagely.

Reagents	Experiment	Iron concentration in aqueous phase (ppm)	Average (ppm)	Removal Percentage (%)
D.W	1	0.015	0.12	1.20
	2	0.345		
	3	0		
Maleic acid	1	9.080	9.48	94.79
	2	10.38		
	3	8.977		
Formic acid	1	0.367	0.17	1.65
	2	0.128		
	3	0		
EDTA disodium salt	1	6.085	8.65	86.48
	2	9.707		
	3	10.1532		
Citric acid	1	10.7604	10.55	105.48
	2	10.232		
	3	10.6522		
Fumaric acid	1	0.624	0.43	4.26
	2	0.655		
	3	0		
Succinic acid	1	0.135	0.26	2.64
	2	0.137		
	3	0.519		
Glutaric acid	1	0.124	0.09	0.91
	2	0.148		
	3	0		

Table 3. The removal percentage (%) after reaction with $Fe(TMHD)_3$
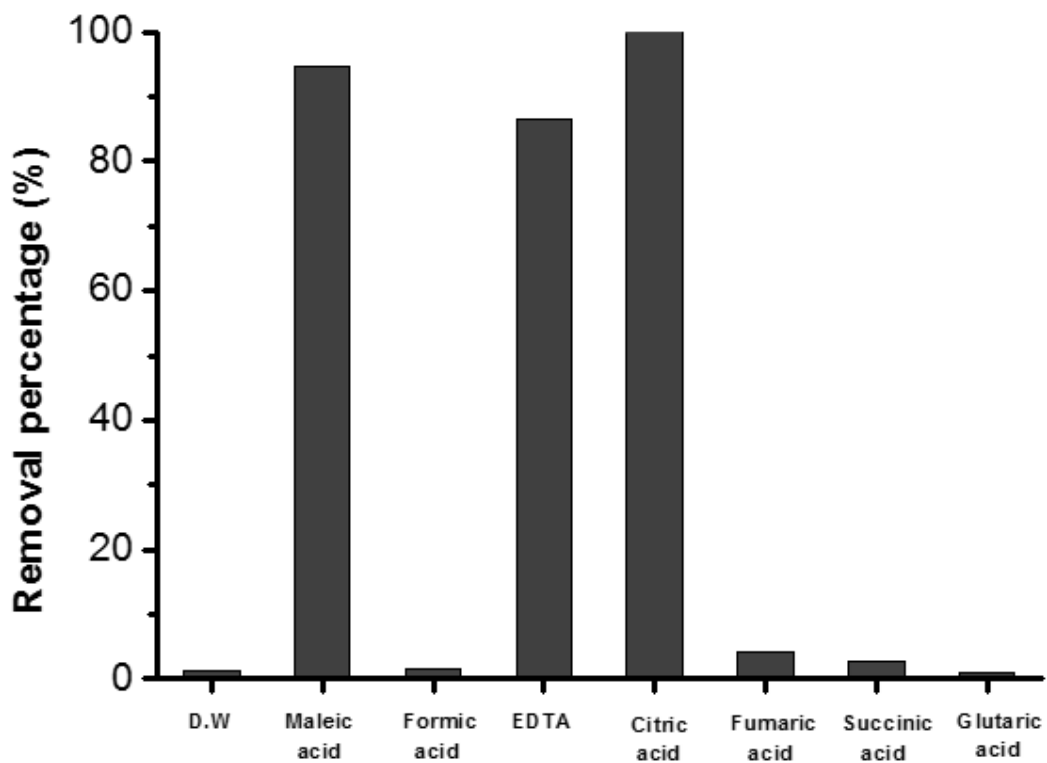
Figure 5. Removal percentage of iron from iron (III) tris (2,2,6,6-tetramethyl-3,5-heptanedionate)

2. Discussion

We conducted reaction with model compounds such as iron standard solution (1,000 μg/g, in 75 cSt hydrocarbon oil, iron (III) 2-ethylhexanoate and iron (III) tris (2,2,6,6-tetramethyl-3,5-heptanedionate). We used several organic acids such as formic acid, maleic acid, fumaric acid, succinic acid, glutaric acid, citric acid and ethylenediaminetetraacetic acid (EDTA) disodium salt.

The solubility of citric acid is much greater than that of other acids, and the iron removal ability was also great than other acids. Maleic acid and fumaric acid also have good solubility in water, about 500 grams per 1 liter of water, but only maleic acid showed positive results in iron removal. And, we used ethylenediaminetetraacetic acid (EDTA) disodium salt, dihydrate, instead of ethylenediaminetetraacetic acid (EDTA) because the solubility of sodium salt form is much greater than that of free acid form. Ethylenediaminetetraacetic acid (EDTA) disodium salt, dehydrate showed rather high value of solubility about 96 grams per 1 liter of water, and the ability of iron removal was also great. The solubility of fumaric acid and succinic acid was rather poor than other acids, and the removal ability of these acids was also not great.

In other words, organic acids having good solubility in water such as maleic acid, ethylenediaminetetraacetic acid (EDTA) disodium salt, and citric acid showed best result for iron removal. However, it is rather rash conclusion that solubility parameter directly affect the ability of iron removal. So we anticipated that the number of functional groups and the conformation of the molecules may affect the ability in iron chelation.

As I've already mentioned, the carboxyl group can produce H+ ion and this H+ ion can be exchanged with iron from several organoiron complexes. And as well as carboxyl group, hydroxyl group can also have influence in reacting with iron. [6] Hydroxyl group can also produce H+ ion and this H+ ion can be exchanged with iron. In this way, carboxyl group and hydroxyl group will be the binding cite of iron and the number of these kind of functional group would be affect the removal efficiency of iron.

Formic acid has only one carboxyl group, and citric acid has three carboxyl groups and one hydroxyl group. In the case of formic acid having only one carboxyl group, there was no successful result in iron removal, but when using citric acid, which have a lot of functional groups, it showed remarkable results in removal efficiency of iron. And it is also known that citric acid reacts with iron forming iron−dicitrate

complexes. [7]

  I've also used ethylenediaminetetraacetic acid (EDTA) disodium salt
and it showed great results. It is a well-known chelating agent for iron
having four carboxyl groups which can chelate metal ions. In other
words, organic acids which have a lot of functional group is effective
for removal of iron from organoiron complexes.

  And also, in the case of ethylenediaminetetraacetic acid (EDTA)
disodium salt, the stability constant of iron (II) and iron (III) with EDTA
disodium salt is 14.3 and 25.7, respectively. Those are much higher
values compared to other common organic acids. The stability constant
of iron (II) and iron (III) with citric acid is 3.2 and 11.85, respectively.
It is rather low value compared to EDTA, but citric acid also showed
great results in removal of iron from model compounds.

  In the case of maleic acid, fumaric acid and succinic acid, there were
also interesting results in removal efficiency of iron from three
different model compounds. Maleic acid and fumaric acid are *cis/trans*
isomer of dicarboxylic acid having four carbon backbone and one double
bond inside the chain. Surprisingly, only maleic acid showed great
ability of iron removal and the latter did not. Maleic acid has *cis*-
conformation and this conformation would be more effective in making
complex with iron metal than fumaric acid which has *trans*-

conformation. It can be explained by coordination chemistry of iron chelation. According to the preferred coordination number, iron can be chelated by 6 oxygens making octahedral complexes, and this is the most stable conformation in iron chelation. When using maleic acid, two carboxyl groups in one molecule can bind to iron simultaneously, because of its *cis*-conformation, and only three molecule is needed to make an iron-maleate complex. [8] However, in the case of fumaric acid, the two carboxyl groups in one molecule can't bind to iron simultaneously, and only one carboxyl group in a molecule can bind to iron, because of its *trans*-conformation. This means that six molecules of fumaric acids are needed to make an iron-fumarate complex. In other words, iron-fumarate complexes are hardly formed, so fumaric acid is not effective in removal of iron from iron model compounds. When using succinic acid, which is saturated dicarboxylic acid consist of four carbon backbone, the results were not successful. I anticipated that succinic acids would show better results than fumaric acid, in other words, it can rotate more freely than fumaric acid because there is no double bond inside the chain. However, the removal efficiency of succinic acid was not much better than that of fumaric acid and almost no iron was removed from three different model compound solutions. As a result, the existence of double bond does not have influence on

removal efficiency of iron from model compounds.

4. Conclusion

 We tested the possibility about removal of iron from three different model compounds using several organic acids. As a result, maleic acid, citric acid and ethylenediaminetetraacetic acid (EDTA) disodium salt showed best results for removal of iron from three different model compounds such as iron standard solution, iron (III) 2-ethylhexanoate and iron (III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate).

 The removal effiency of iron from model compounds depends on the number of functional groups such as carboxyl group and hydroxyl group. In other words, organic acids which have a lot of functional groups such as citric acid and ethylenediaminetetraacetic acid (EDTA) disodium salt were effective in iron removal..

 As well as the number of functional groups, the conformation of molecules is also an important factor in deciding the chelating ability with iron. We used maleic acid and fumaric acid which are *cis/trans* isomer of dicarboxylic acid having four carbon backbone and one double bond inside the chain. As a result, only maleic acid showed great results because of its *cis*-conformation. And fumaric acid which has *trans*-conformation didn't show great result in removal of iron form all model compounds. We also tested succinic acid, but the reaction was not

successful, in other words, no iron was removed from model compounds.

Experimental Details

General procedure

Iron standard solution (1,000 μg/g, in 75 cSt hydrocarbon oil) was purchased from Agilent. Iron (III) 2-ethylhexanoate and iron (III) tris (2,2,6,6-tetramethyl-3,5-heptanedionate) (Fe(TMHD)$_3$) were purchased from Alfa aesar.

All of the chemicals were used without further purification. It can be assumed that minor impurities would have a little effect on the data. All of the glassware, magnetic stirring bars used in this paper were dried in oven before usage.

Preparation of 10 ppm solution of iron standard solution (1,000 **μg/g**, in 75 cSt hydrocarbon oil)

 1 g of iron standard solution (1,000 **μg/g**, in 75 cSt hydrocarbon oil) was diluted with 99 g of xylene to make a 10 ppm solution of iron standard solution. This solution was stored in a 200 mL bottle.

Preparation of 5 ppm solution of iron (III) 2-ethylhexanoate

0.616 g of iron (III) 2-ethylhexanoate, nominally 50% in mineral spirits (0.09 mmol), was dissolved in 299.384 g of xylene to make a 10 ppm solution of iron (III) 2-ethylhexanoate. This solution was stored in a 500 mL bottle.

Preparation of 10 ppm solution of iron (III) tris (2,2,6,6-tetramethyl-3,5-heptanedionate) (Fe(TMHD)$_3$)

 1.090 g of iron(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate) (1.80 mmol) was dissolved in 298.910 g of xylene to make a 10 ppm solution of iron(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate). This solution was stored in a 500 mL bottle.

Preparation of 6 mM aqueous solution of maleic acid

0.042 g of maleic acid (0.36 mmol) was dissolved in 59.958 g of distilled water to make a 6 mM aqueous solution of maleic acid. This solution was stored in 70 mL vial.

Preparation of 6 mM aqueous solution of citric acid

0.069 g of maleic acid (0.36 mmol) was dissolved in 59.931 g of distilled water to make a 6 mM aqueous solution of citric acid. This solution was stored in 70 mL vial.

Preparation of 6 mM aqueous solution of succinic acid

0.043 g of succinic acid (0.36 mmol) was dissolved in 59.957 g of distilled water to make a 6 mM aqueous solution of succinic acid. This solution was stored in 70 mL vial.

Preparation of 6 mM aqueous solution of fumaric acid

0.042 g of succinic acid (0.36 mmol) was dissolved in 59.958 g of distilled water to make a 6 mM aqueous solution of fumaric acid. This solution was stored in 70 mL vial.

Preparation of 6 mM aqueous solution of glutaric acid

0.048 g of succinic acid (0.36 mmol) was dissolved in 59.952 g of distilled water to make a 6 mM aqueous solution of glutaric acid. This solution was stored in 70 mL vial.

Preparation of 6 mM aqueous solution of ethylenediaminetetraacetic acid (EDTA) disodium salt dehydrate.

0.134 g of succinic acid (0.36 mmol) was dissolved in 59.866 g of distilled water to make a 6 mM aqueous solution of ethylenediaminetetraacetic acid (EDTA) disodium salt dehydrate. This solution was stored in 70 mL vial.

Preparation of 10 mM aqueous solution of formic acid

0.017 g (0.014 mL) of conc. (99%) formic acid (0.60 mmol) was dissolved in 59.983 g of distilled water to make a 10 mM aqueous solution of formic acid. This solution was stored in 70 mL vial.

Experiment of iron standard solution (1,000 μg/g, in 75 cSt hydrocarbon oil) with distilled water.

5 g of iron standard solution (1,000 μg/g, in 75 cSt hydrocarbon oil) was added to 5 g of prepared distilled water. This mixture was stirred for 5 hours at 80 °C, 1500 rpm. After reaction, the mixture was cooled down to room temperature and separated into two phase by using separatory funnel.

The separated aqueous phase was analyzed by Inductively Coupled Plasma−Atomic Emission Spectroscopy (ICP−AES).

Experiment of iron standard solution (1,000 μg/g, in 75 cSt hydrocarbon oil) with aqueous solution of chemical reagents.

5 g of iron standard solution (1,000 μg/g, in 75 cSt hydrocarbon oil) was added to 5 g of prepared aqueous solution of chemical reagents. This mixture was stirred for 5 hours at 80 °C, 1500 rpm. After reaction, the mixture was cooled down to room temperature and separated into two phase by using separatory funnel.

The separated aqueous phase was analyzed by Inductively Coupled Plasma−Atomic Emission Spectroscopy (ICP−AES).

Experiment of iron (III) 2−ethylhexanoate with distilled water.

5 g of iron (III) 2−ethylhexanoate was added to 5 g of prepared distilled water. This mixture was stirred for 5 hours at 80 °C, 1500 rpm. After reaction, the mixture was cooled down to room temperature and separated into two phase by using separatory funnel.

The separated aqueous phase was analyzed by Inductively Coupled Plasma−Atomic Emission Spectroscopy (ICP−AES).

Experiment of iron (III) 2-ethylhexanoate with aqueous solution of chemical reagents.

5 g of iron (III) 2-ethylhexanoate was added to 5 g of prepared aqueous solution of chemical reagents. This mixture was stirred for 5 hours at 80 ℃, 1500 rpm. After reaction, the mixture was cooled down to room temperature and separated into two phase by using separatory funnel.

The separated aqueous phase was analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

Experiment of crude oil with distilled water.

4g of crude oil was diluted with 1 g of xylene and added to 5 g of distilled water. This mixture was stirred for 5 hours at 80 ℃, 1500 rpm. After reaction, the mixture was cooled down to room temperature and separated into two phase by using separatory funnel. The separated aqueous phase was analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

Experiment of crude oil with aqueous solution of chemical reagents.

4g of crude oil was diluted with 1 g of xylene and added to 5 g of aqueous solution of chemical reagents. This mixture was stirred for 5 hours at 80 ℃, 1500 rpm. After reaction, the mixture was cooled down to room temperature and separated into two phase by using separatory funnel. The separated aqueous phase was analyzed by Inductively Coupled Plasma－Atomic Emission Spectroscopy (ICP－AES),

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국문 초록

원유 내에는 철, 바나듐, 니켈 등과 같은 금속성분이 포함되어 있다. 이러한 미량의 금속은 원유 정제 공정에서 부정적인 영향을 미칠 수 있다. 예를 들어, 금속은 원유 처리 플랜트를 부식시킬 수 있고, 열 교환기 내에서 파울링 문제를 발생시킬 수 있다. 이러한 다양한 문제점들 중에서 가장 문제가 되고 있는 것은 촉매 활성 감소이다. 다시 말해서, 원유 내 존재하는 금속은 후단 공정에서 사용되는 촉매의 표면을 덮게 되어 이들의 정상적인 작용을 방해한다. 이러한 이유 때문에, 지난 수십년간 원유 내에 존재하는 금속 제거의 필요성이 증가되고 있는 실정이다.

원유 내에 존재하는 금속 중 무기산화물이나 무기황화물 등의 무기염 형태로 존재하는 경우에는 일부분이 탈염기 공정에 의해 제거될 수 있다. 하지만 대부분의 금속은 금속과 결합하여 복합체를 형성하고 있으며, 이러한 복합체는 친유성이며 물에 대한 용해도가 좋지 않아 탈염기 공정에서 쉽게 제거되지 않는다.

철의 경우 역시 원유 내에서 다양한 유기물질과 결합하고 있다. 우리는 유도결합플라즈마-원자방출분광법 (ICP-AES)에 사용되는 철 표준물질과 아이런(II) 2-에틸헥사노에이트, 아이런 (III) 트리스 (2,2,6,6-테트라메틸-3,5-헵탄다이오에이트) 를 모델화합물로 선정하였다. 이러한 모델컴파운드를 다양한 유기산과 함께 반응시켜 보았다. 그 결과, 구연산, 이디티에이와 같은 유기산을 사용하였을 때

모델화합물로부터의 확연한 철 제거효과를 확인하였다. 말레산 역시 철 제거에 효과를 보이며 긍정적인 가능성을 보여주었다.