CHEMISTRY

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SYNTHESIS OF IMIDAZOLINE COMPLEXES ON THE BASIS OF DIETHYLENETRIAMINE AND NAPHTHENIC ACID FRACTIONS WITH SUBSEQUENT ORGANIC ACID TREATMENT AND RESEARCH OF IMIDAZOLINE COMPLEXES AS CORROSION INHIBITOR

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Abstract

Purpose of this study is synthesis of nitrogen organic compounds, which are water soluble and highly effective polyfunctional inhibitors. As nitrogen organic compounds, imidazoline derivatives synthesized on the basis of diethylenetriamine (DETA) and various fractions of naphthenic acids derived from Caspian origin crude oil. Synthesized imidazolines treated with formic acid and acetic acid for preparation of end-product complexes, which are water soluble. Effect of the complexes on metal corrosion was investigated for solutions containing H_2S and CO_2 at low pH environment. It is concluded that the inhibitor-complexes start showing high inhibition efficiency at their concentration being 10 mg/L in H_2S medium and 25mg/L in CO_2 medium.

Keywords: acetic acid, formic acid, inhibitor efficiency

INTRODUCTION

Carbon dioxide and hydrogen sulphide corrosion of carbon steel pipelines and equipments leads to damage to oil and gas sector equipments. [1,2]. Corrosion lead to reduction in utilization period of equipments, loss of production and in some cases also lead to undesired environmental impact. Therefore, there is high demand for oil and gas sector equipments regarding material of construction and anti-corrosion measures. Use of corrosion inhibitor is widespread and is effective way against internal corrosion. There is wide range of corrosion inhibitors, whereas each type generally specializes for certain conditions. Polyfunctionality of corrosion inhibitors present high importance when it comes to use them in complex mediums, such as systems containing CO_2, H_2S with water at low pH [1-5].

It is well known fact that, nitrogen organic compounds are used in acidic medium as corrosion inhibitors. Their action mechanism is based on forming stable inhibition layer on the metal surface, which protects attack of corrosive agents into the metal surface. Formation of the layer is due to chemical adsorption of nitrogen organic compounds onto the metal surface. One of the most effective type corrosion inhibitors used for oil field applications are imidazoline type compounds[4,5,6]. Considering all the above, for synthesis of corrosion inhibitors showing high performance in H_2S and CO_2 containing acidic mediums, imidazoline derivatives synthesized on the basis of Diethylenetriamine (DETA) and naphthenic acid fractions which were extracted from Baku oils.

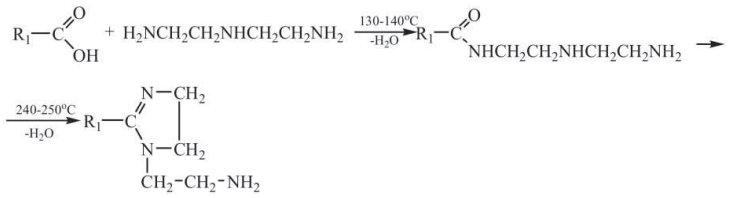
1) Experimental process

Naphtenic acid extracted from Baku oil. Naphthenic acid (NA) mixture fractionated into following 4 fractions based on TBP values: 270-320°C, 320-350°C, 350-380°C, above 380°C. Their physico-chemical properties are given in below table 1.

Table 1. Physico-chemical properties of Naphthenic acid fractions

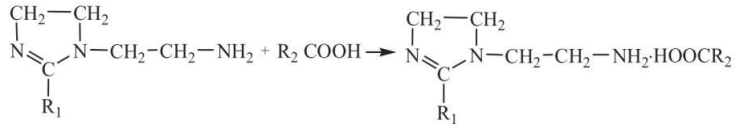
NA fractions	TBP, °C	Tboil, °C (Vacuum) 4-5 mm.hg	Acid Number, mg KOH/g	Average Molecular Weight, g/mole
I	270-320	110-150	277,3	202
II	320-350	150-175	274,3	204,5
III	350-380	175-200	240,5	233,3
IV	Above 380°C	Above 200°C	216,5	259

Experiments carried out for synthesis of imidazoline complexes from DETA and naphthenic acid fractions. Reactions were performed in three-neck flask which was provided by reverse cooling. O-xylene (50 ml) was added into the flask where 0.11 mole naphthenic acid fraction (I) was initially placed. The reaction medium was brought to 80°C and 0.11 mole DETA was added into the mixture gradually. After DETA was added, temperature was increased to 130-140°C and kept for 2.5 hours. Water formed as result of the reaction removed by o-xylene by accumulating in Dean-Stark unit. Amides formed as a result of above explained 1.step of the reaction. Second step of the reaction carried out at elevated temperatures being 240-250 for 3 hours which yielded imidazoline as main product. Water removed from reaction medium. Scheme of the reaction is given in scheme 1.



Scheme 1. Synthesis of imidazoline derivatives from Naphthenic acid and DETA

Synthesis of imidazoline derivatives from NA II and III fractions were carried out by the same experimental methods. As second step, imidazoline derivatives, which have been synthesized from DETA and NA factions, put into reaction with 100% acetic acid and 85% formic acids, leading formation of water soluble complexes. Reaction was carried at ambient temperature with mixing two substances. Yield of the end product complexes were given in below table 2:



Scheme 2. Imidazoline complex formation process of imidazoline derivatives with formic and acetic acid. R2 = H, CH_3

Table 2. Yield of Imidazoline complexes based on DETA, Naphthenic Acid fractions and organic acids.

Synthesized Inhibitor reagent	Yield of product, %
DIMDZ(I)+HCOOH (1:1 mol. ratio)	97,4
DIMDZ (II)+HCOOH (1:1 mol. ratio)	99,8
DIMDZ (III)+HCOOH (1:1 mol. ratio)	97,5
DIMDZ (I)+CH3COOH (1:1 mol. ratio)	100
DIMDZ (II)+CH3COOH (1:1 mol. ratio)	97,5
DIMDZ (III)+CH3COOH (1:1 mol. ratio)	100

IR spectrum of complexes were analyzed and one example given below as evidence that complexes actually were synthesized as per above reactions.

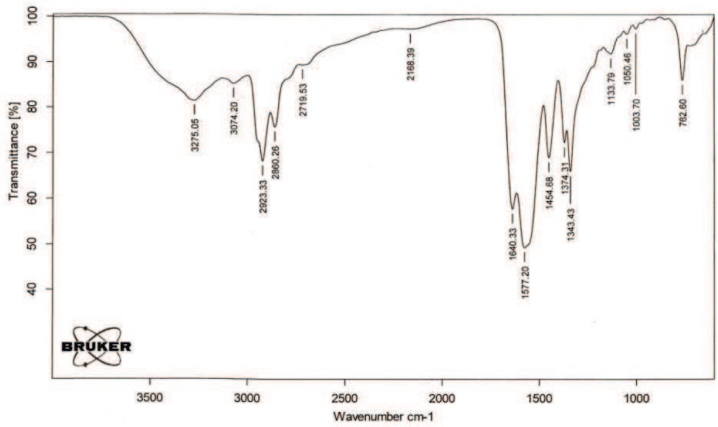


Figure 1. IR spectrum of DETA based imidazoline complex with formic acid

IR spectrum of imidazoline derivatives was analyzed. There are following absorption bonds of imidazoline and formic acid complex on IR-spectrum: ν =2923 sm-1 compatible to C-H bonds of CH_2 group; C-H δ =1454 cm-1 of CH_3 group; NH ν =3275 cm-1; C-N ν =1003; 1050; C═N ν=1577cm-1; NH_3^+ ν =2168 cm-1; 2719 cm-1;

2) Discussion of results

Analyses carried out regarding inhibition properties of synthesized imidazoline derivatives and their complexes with acetic and formic acid against corrosion in CO_2 medium. Studies executed by ACM GILL AC trademark potentiometer which equipped with ACM program. The program gives output which is dependence graph of corrosion rate from time. Initially prepared 1% NaCl aqueous solution was saturated by CO2 at 9 barg source pressure and gas injection continued till the end of experiment [4-7].

Corrosion rates of electrodes (made of C1018 type steel) studied for empty and for system comprising imidazoline salts under 50^{o}C temperature for 20 hours. According to the results of potentiometer, following values calculated: adsorption constant, Gibbs energy value, surface coverage indices and inhibitor efficiency values. Results are given in below table 2 and table 3.

Table 2. Results of Corrosion Inhibition analysis of imidazoline complexes of DETA and NA fractions which is carried in CO_2 enriched medium

Synthesized Inhibitor reagent	Concentration (mg/l)	Rate of Corrosion, ρ mm/y	Delay Coefficient, γ	Inhibitor Efficiency, Z %
DIMDZ(I)+HCOOH	25 50 100	0,57 0,46 0,1	6,0 7,5 34,5	83,7 86,8 97,1
DIMDZ (II)+HCOOH	25 50 100	1,06 0,54 0,16	3,2 6,4 21,4	69,0 84,3 95,3
DIMDZ (III)+HCOOH	25 50 100	0,154 0,1 0,06	22,2 34,3 57,2	95,5 97,1 98,5
DIMDZ (I)+CH_3COOH	25 50 100	0,262 0,1 0,08	13 34,3 42,9	92,4 97,1 97,6
DIMDZ (II)+CH_3COOH	25 50 100	0,293 0,103 0,05	11,7 33,3 68,6	91,5 96,9 98,5
DIMDZ (III)+CH_3COOH	25 50 100	0,28 0,11 0,05	12 31,2 68,6	91,8 96,7 98,5

As seen from results, for all three NA fractions, complexes produced with acetic acid show slightly higher inhibition effect than the complexes which yielded with formic acid. It can be also safely concluded that, imidazoline complexes synthesized from heavy naphthenic acid fraction (III) show better performance compare to lighter ones. As, ‘’DIMDZ (III)+HCOOH’’ at 100 ppm concentration show 98,5% inhibitor efficiency, whereas ‘’ DIMDZ (I)+HCOOH‘’ give 97,1% inhibitor efficiency.

Table 3. Physico-chemical characteristics of inhibition process of imidazoline complexes of DETA and NA fractions which is carried in CO_2 enriched medium

Synthesized Inhibitor reagent	Concentration (mg/l)	Time, hour	Surface coverage index, θ	Adsorption constant K_{ads}, $M*10^{-4}$	Gibbs energy ΔG ads kJ/mol-1
DIMDZ(I)+HCOOH	25	20	0,834	6,3	-36
	50		0,866	4,1	-37
	100		0,97	10,5	-38,6
DIMDZ (II)+HCOOH	25	20	0,955	27	-40
	50		0,971	21	-40,5
	100		0,983	17,8	-41
DIMDZ (III)+HCOOH	25	20	0,915	14,8	-39,4
	50		0,971	23	-40,5
	100		0,985	23,4	-40,7
DIMDZ (I)+CH_3COOH	25	20	0,691	3,0	-35
	50		0,843	3,5	-36
	100		0,953	6,7	-37,5
DIMDZ (II)+CH_3COOH	25	20	0,924	16	-39,3
	50		0,971	22	-39,6
	100		0,977	14	-40,4
DIMDZ (III)+CH_3COOH	25	20	0,918	16,2	-39,7
	50		0,968	21,7	-40,4
	100		0,985	24,3	-42,5

Complex of acetic acid in 1:1 molar ratio with Imidazoline derivative, which obtained from reacting DETA and NA (I fraction), analyzed regarding its effect on kinetics of steel corrosion in CO_2 medium and results are given in below figure 1.

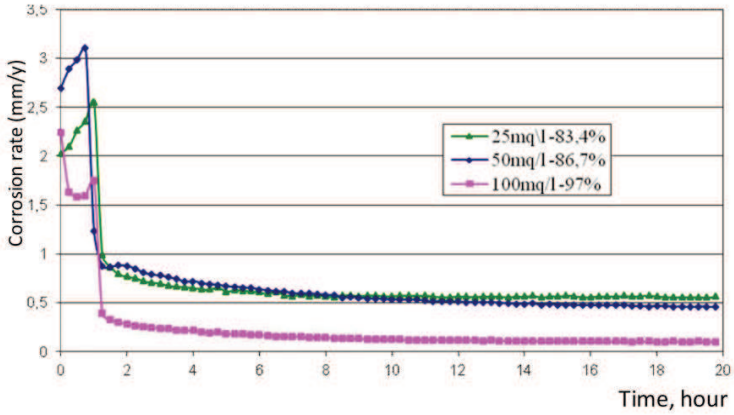


Fig 1. Effect of imidazoline complex, which obtained from DETA and NA (I fraction) & formic acid on kinetics of steel corrosion for CO_2 saturated 1% NaCl solution

As seen from above graphics, inhibitor complex demonstrates less than 90% inhibition efficiency for 25 ppm and 50 ppm concentrations. At 100 ppm concentration, the complex shows

97% inhibition efficiency, which is appropriate according to requirements for effective corrosion inhibitors.

Effect of imidazoline complexes in H_2S containing environment was studied. For this purpose, water and kerosene mixture was prepared and system saturated with 500 ppm H_2S afterwards. Steel plate was put into mixture and mixture continuously mixed for homogenous environment. Experiment carried out without inhibitor and with inhibitor case. Various inhibitor complexes and their different concentrations were used for experiments. Gravimetric methodology applied for calculation of metal loss and consequent calculation of physical-chemical properties.

Table 3. Results of Corrosion Inhibition analysis of imidazoline complexes of DETA and NA fractions which undertaken in H_2S enriched medium

Synthesized Inhibitor reagent	Concentration (mg/l)	Surface coverage index, θ	Adsorption constant Kads, M-1·104	Gibbs energy ΔG ads kJ/mol-1
DIMDZ (I) +HCOOH	10	0,92	37,9	-41,4
	25	0,98	73	-41,8
	50	0,98	40	-42
	100	0,99	32	-43,4
DIMDZ (I) +CH_3COOH	10	0,95	76	-42
	25	0,98	67	-43,2
	50	0,98	43	-43,5
	100	0,99	86	-43,8
DIMDZ (II) +HCOOH	10	0,98	159	-45,3
	25	0,99	328	-45,5
	50	0,99	235	-46
	100	0,99	173	-47
DIMDZ(II)+CH_3COOH	10	0,98	213	-45,5
	25	0,99	493	-46
	50	0,99	346	-47
	100	0,99	172	-48
DIMDZ (III) +HCOOH	10	0,97	151	-43
	25	0,97	58	-44
	50	0,99	92	-45
	100	1	-	-
DIMDZ(III)+CH_3COOH	10	0,97	133	-45
	25	0,99	186	-45,7
	50	0,99	199	-46
	100	1	-	-

For all analyzed concentrations of complexes, which effect checked in CO_2 saturated 1% NaCl aqueous solution, Gibbs energy was found to be in the range of - 42.5 – (-36) kJ/mole and in H_2S environment was found to be in the range -41.4 - (-48) which indicate that the complexes form stable adsorption layer on the metal surface in both CO_2 and in H_2S mediums.

3) maın Conclusions

1. Imidazoline derivatives synthesized on the basis of diethylenetriamine and Baku section Caspian oil naphthenic acids.

2. Imidazoline derivatives reacted with acetic acid and formic acid for preparation of complexes and corrosion inhibition characteristics of the complexes were studied.

3. Adsorption characteristics of the complexes were analyzed. High K_{ads} and low Gibbs energy of complexes show evidence of high adsorption capability of the synthesized complexes on metal surface.

4. Inhibition effectiveness of imidazoline complexes increase as per increase of boiling point range of naphthenic acid fractions, which is believed to be due to long oleic chain of heavy naphthenic acid fractions.

5. Imidazoline complexes with acetic acid show better performance compare to formic acid.

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