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Synthesis of imidazoline derivatives on the basis of triethylenetetramine and naphthenic acids and research of imidazoline derivatives as corrosion inhibitor

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Abstract. ***In this paper, imidazoline compounds are proposed for crude oil pipeline protection against corrosive agents in crude oil. Imidazoline were synthesized on the base of triethylenetetramine and naphthenic acids. Synthesized imidazoline treated with formic acid for preparation of end-product complexes. Effect of the complexes on metal corrosion was investigated for solutions containing CO_2 and H_2S, both systems being acidic medium. It is concluded that the inhibitor-complexes start showing high inhibition efficiency at their concentration being 25 mg/L in CO_2 medium and 10 mg/L in H_2S medium.***

Key words: **naphthenic acids, triethylenetetramine, corrosion inhibitor, Langmuir isotherm.**

I. INTRODUCTION

Exploration and Production from oil and gas wells containing crudes with high amount of CO_2 and H_2S, leads to corrosion of oil and gas sector equipments. Corrosion leads to decreased amortization times of equipments and also unplanned shutdowns. Therefore, there are extensive and intensive demands for oil and gas sector equipments regarding material of construction and corrosion protection measures. One of the widespread and efficient methods used for fighting against corrosion is application of corrosion inhibitors. Industry exploits wide range of corrosion inhibitors, whereas each type generally specializes for certain conditions. In some instances, selected corrosion inhibitor fails to function properly either due to change in process conditions or due to lack of polyfunctionality [1-4]. 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 [5,6]. Considering all the above, for synthesis of corrosion inhibitors showing high performance in CO_2 containing acidic mediums, imidazoline derivatives synthesized on the basis of Triethylenetetramine (TETA) and various fractions of naphthenic acids which was extracted from Baku oils.

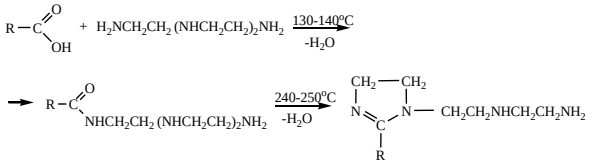
II. EXPERIMENTAL PROCEDURE

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. Naphthenic acid fractions and physico-chemical properties

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 TETA and NA (Naphthenic Acids) 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 mol. NA (I frack.) was initially placed. The reaction medium was brought to 80°C and 0.11 mol TETA was added into the mixture gradually. After TETA was added, mixture's 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.



Scheme 1. Synthesis of imidazoline derivatives. R-five or six membered naphtene hydrocarbon's part; consist of phenyl and alkyl radicals

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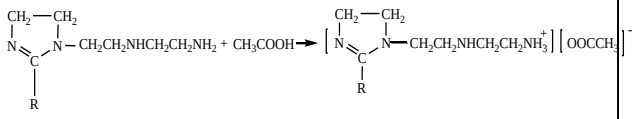
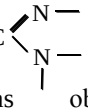
Water removed from reaction medium. Total imidazoline yield of the reaction was quite satisfactory, which recorded to be 93.5%. Scheme of the reaction is given in scheme 1.

Synthesis of NA number II and III fractions for producing imidazoline derivatives were carried out by the same experimental methods. As second step, imidazoline derivatives, which have been synthesized from TETA and NA factions, put into reaction with 100% acetic acid, leading formation of water soluble complexes. Reaction was carried out both 1:1 and 1:2 molar ratios and performed at ambient temperature with mixing two substances.



Scheme 2. Formation of complexes with imidazoline derivatives and acetic acid

NMR and IR spectrum of imidazoline derivatives was analyzed. NA: NMR-1H 300, 18 MHz "Bruker": (CH_2 and CH_3) δ=1,25 - 0,84 ppm; δ=1,4-1,8 ppm naphthenic; δ=6,6-7,4 ppm aromatic hydrocarbons absorption band was identified. Resonance signals  corresponding to H_2 and OH groups of Carboxyl fragments (CH_2-COOH) was observed in δ=2, 1 - 11, 5 ppm value. Deuterium Benzene was used as solvent. Compound TİMDZ 1H NMR: for naphthenic acids alkyl fragments (CH3 and CH2) compatible signals δ = 0,90 - 1,35 ppm; Naphthenic H/Cs δ = 1,50-1,80 ppm; NH_2 δ = 2,20 ppm; CH_2 groups bonded with nitrogen atoms δ = 2,30-3,10 ppm; Ethyl groups absorption band δ = 3,30 -3,60 ppm values were observed. Compound: 1H NMR-spectrum of imidazoline derivatives and acetic acid complex: the signals compatible to the protons in CH3 group of oil acid in δ = 0.834 ppm, the signals belonging to -CH2-NH- groups in δ = 1.2-2.98 ppm, the signal belonging to was observed in δ = 7.8 ppm values. 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 =1374 cm-1 of CH_3 group; ν =2817; 2853 cm-1; NH δ =1552; ν =3292 cm-1; C-N ν =1010; 1128; 1266; 1304 cm-1; C=N ν=1646 cm-1; NH3+ ν =2155 cm-1; 2681 cm-1; COO- δ =1591 cm-1.

III. RESULTS AND DISCUSSION

Analyses carried out regarding inhibition properties of synthesized imidazoline derivatives and their complexes with acetic acid against corrosion in CO_2 medium. Studies executed 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 under condition of 9 barg source pressure and gas injection continued till the end of experiment [7,8]. Corrosion rates of electrodes (made of C1018 type steel) studied for empty and for system comprising imidazoline salts under 50oC temperature for 20 hours. According to the results of potentiometer, following values calculated: adsorption constant, Gibbs energy value, surface coverage indices and protective effect values. Results are given in below table 2.

Synthesized Inhibitor reagent	Concentration (mg/l)	Time, hour	Rate of Corrosion, mm/year	Surface coverage index, θ	Adsorption constant Kads, M-1· 104	Protective effect Z, %	Gibbs energy ΔG ads kJ/mol-1
Without inhibitor	-	20	3,43	-	-	-	-
TIMDZ(I)+CH3COOH (1:1 mol. ratio)	25 50 100	20	0,82 0,31 0,18	0,691 0,843 0,953	3,0 3,5 6,7	76 91,0 94,7	-35 -36 -37,5
TIMDZ (I)+CH3COOH (1:2 mol. ratio)	25 50 100	20	0,81 0,24 0,12	0,764 0,93 0,965	5,6 11,5 11,9	76,7 93,0 96,5	-37 -39 -39
TIMDZ (II)+CH3COOH (1:1 mol. ratio)	25 50 100	20	0,82 0,177 0,177	0,924 0,971 0,977	16 22 14	75,9 94,8 94,8	-39,6 -40,4 -39,3
TIMDZ (II)+CH3COOH (1:2 mol. ratio)	25 50 100	20	0,247 0,151 0,051	0,928 0,956 0,985	22,319 28,8	92,7 95,5 98,5	-40,4 -40 -41
TIMDZ (III)+CH3COOH (1:1 mol. ratio)	25 50 100	20	0,251 0,115 0,069	0,918 0,968 0,985	16,2 21,7 24,3	92,6 96,6 98,0	-39,7 -40,4 -40,7
TIMDZ (III)+CH3COOH (1:2 mol. ratio)	25 50 100	20	0,22 0,07 0,056	0,936 0,98 0,984	25,341,726	93,3 98,2 98,5	-40,7 -42 -41

Table 2. Results of Corrosion Inhibition analysis of imidazoline complexes of TETA and NA fractions which undertaken in CO2 medium

As seen from results, for all three NA fractions, complexes which produced with 1:1 molar ratio show lower inhibition effect than the complexes which yielded with 1:2 molar ratios. Complex of acetic acid in 1:1 molar ratio with Imidazoline derivative, which obtained from reacting TETA and NA (I fraction), analyzed regarding its effect on kinetics of steel

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corrosion in CO_2 medium and results are given in below figure 1.

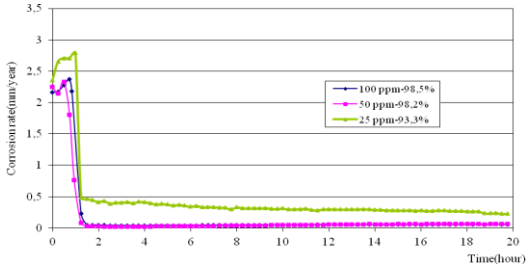

Fig 1. Effect of imidazoline, which formed from TETA and NA (I fraction), on kinetics of steel corrosion for CO2 saturated 1% NaCl solution

In below figure 2, for the complex TIMDZ (II) + CH_3COOH (1:1 molar ratio) different concentrations, relation of metal loss from time in CO_2 medium is given.

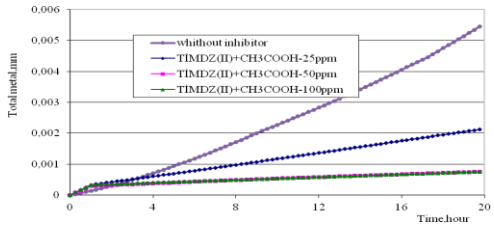

Fig 2. For the system utilizing complex TIMDZ (II) + CH_3COOH (1:1 molar ratio) as inhibitor in CO_2 medium, dependence of metal loss from time given, which analysis carried out for C1018 type steel plate.

As seen from graphs in figure 2, medium containing corrosion inhibitor metal loss substantially decreases for the case when no inhibitor is added. Hence, for 20 hours of experimenting metal loss with no inhibitor case is 0,0054mm, whereas with inhibitor's concentration of 25, 50, 100 ppm, metal loss values respectively are 0,002 mm, 0,000753 mm, 0,000754 mm. Langmuir isotherms are given in Fig3.

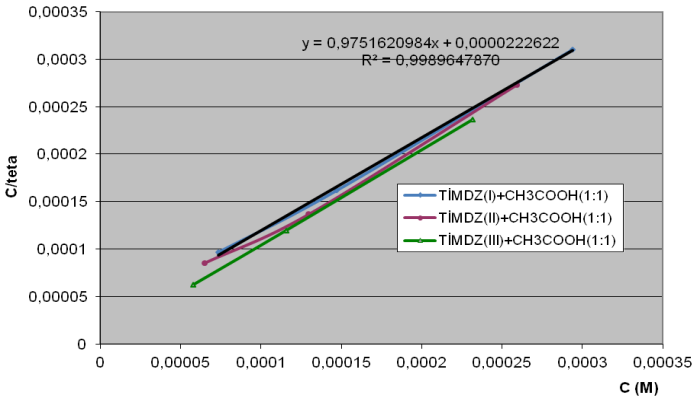

Fig 3. Langmuir isotherms of TIMDZ complexes with Naphthenic Acid (I, II & III fractions)

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 – (-35) kJ/mole, which indicates that the complexes form stable adsorption layer on the metal surface.

IV. CONCLUSION

1. Imidazoline derivatives synthesized on the basis of triethylenetetramine and Baku oil naphthenic acids.
2. Imidazoline derivatives reacted with acetic acid for preparation of complexes and corrosion inhibition characteristics of the complexes were studied.
3. Adsorption features of the complexes were analyzed. High K_{ads} indicated high adsorption capability of the synthesized complexes on metal surface.

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