PRJ, Vol. 5 (January 1993); P. 67–75, 5 FIGS, 6 TABLES.

SYNTHESIS AND STUDY OF DIFFERENT THIOAMIDES AS CORROSION INHIBITORS

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تخليق ودراسة مواد تياميدية مختلفة لإستعمالها كمانعة للتآكل

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لكثير من المركبات العضوية ذرات تركيبية غنية بالألكترونات، مثال النيتروجين والكبريت، وهي تستعمل بكثرة كمواد مخففة للإحتكاك في الصناعات النفطية وذلك للتقليل من ظاهرة التآكل. ويزيد وجودالذرات الغنية بالألكترونات بجزئيات المركبات تحت الدراسة في رفع قدرتها على تكوين روابط تشاركية متناسقة مع ذرات الفلز ذات العلاقة ببيئة التآكل.

والمركبات المبنية على الأمين الدهني والأمين العطري والإيمادازول والديميدازول والأميد الدهني مواد واسعة الإنتشار كموانع للتآكل في مجال النفط.

وقد تمت في الدراسة تخليق بعض الفينالمسيتياميدات والبنزسيتاميدات. كما وصفت المعلومات الكيميائية والفيزيائية. وقيست معاملات الذوبان والثبات البارد والثبات الساخن وخصائص منع التآكل للمركبات المخلقة تحت ظروف صناعية (10 % خام في ملوحة صناعية عند معامل PH بين 4.5 و74.8، كما تمت مقارنة خصائص مقارنة التآكل ببعض التيميدات المخلقة في تركيزات مختلفة من الملوحة المرتفعة ومياه البحر). وتختلف التميدات المعدة في وزنها الجزئي وذلك لوجود بعض المكونات العضوية المختلفة على مجموعة التيوميدات. وقد بنيت عملية تخليق المركبات المذكورة على تفاعل ولجرودت — كندلر.

وتم التأكد من عملية تخليق المركبات بواسطة العديد من طرق التحليل المعتادة. وقد قورنت القيم التجريبية للتكوين العنصري لهذه المركبات مع القيم المحسوبة ووجدت متناسقة. كما وجد أن قمم منحنيات الإمتصاص المقاس مطيافياً تؤكد وجود مجموعة التيوميد بالمركبات المعدة.

وقد نوقشت في هذه الدراسة ميكانيكية التفاعل المحتملة لتخليق المركبات المذكورة أعلاه، كما تم تفسير ميكانيكية وسبل منع هذه المركبات للتآكل.

ABSTRACT

Many organic compounds having electron rich atoms in their structure, such as nitrogen, and sulphur, are widely in use as lubricating additives in the oil industry to minimise corrosion. The presence of electron rich atoms in the molecules of compounds under discussion, increases the ability of these substances to form co-ordinate covalent bonds with the metal atoms, involved in the corrosion environment.

Compounds based on fatty amine, aromatic amine, imidazoline, di-imidazoline and fatty amide are widely used as corrosion inhibitors. Less attention has been given to study thiocarboxylic acid amides as corrosion inhibitors, in the oil field.

In this work some phenylacetothioamide and benzyl-acetothioamide are synthesised. The chemical and physical data of the prepared compounds are compiled. The solubility, cold stability, heat stability and corrosion inhibition characteristics, of the synthesised compounds have been measured in the artificial environment (10% crude in artificial brine at the pH in between 4.5 to 4.8). Anticorrosive properties for few of the amine based commercially available oilfield corrosion inhibitors and few of the above mentioned synthesised compounds are measured, in the test environment, in order to compare their activity. Prepared thioamides differ in their molecular weights, due to presence of different organic substituents, on the thioamide group. Synthesis of the above mentioned compounds are based on the Willgerodt-Kindler reaction.

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The synthesised compounds are confirmed by IR, UV/Vis, Elemental Analyzer and other traditional analytical techniques. The experimental values of the elemental composition of these compounds were compared with the calculated values and found to be in agreement. UV/Vis and IR spectras also show the absorption peaks, which confirm the presence of thioamide group in the prepared compounds. The possible reaction mechanism regarding the synthesis of the above mentioned compounds is discussed. Mechanism of corrosion inhibition of these compounds in the corrosive environment is explained.

INTRODUCTION

Chemical antidegradants refer to the chemical species which inhibit corrosion of metals and stabilise or adjust the environment in which it has been applied. Corrosion inhibitors form a protective barrier on the surface of a substrate by physical absorption, chemical absorption or reaction with the substrate. Corrosion problems in the operation of petroleum drilling installation are to be solved by the aid of corrosion inhibitors in the injection water. The crude comes out with plenty of minerals containing water. The pH of this aqueous and oily mixture varies but lies on the acidic side. This acidic pH, mineral contents and dissolved gases are responsible for metallic corrosion.

Variety of organic compounds having electron rich atoms in their molecules such as nitrogen and sulphur, are widely used as corrosion inhibitor, because of their anticorrosive and antioxidation properties [1–3]. A large number of these compounds have been synthesised in the Petroleum Research Centre. They showed different percentage composition of nitrogen and sulphur and varying in unsaturations. It has been proved experimentally that higher the molecular weight of the above mentioned types of compounds, higher is the anticorrosive and antioxidation properties. It may be due to more surface area of the molecules. It is also established that the sulphur containing substances are more effective anticorrosive and antioxidative compared to nitrogen containing compounds, provided the molecular weight and molecuar unsaturations are the same [2–3].

Corrosion and oxidation inhibitors are routinely used in oil fields and in the refineries, in order to minimise the corrosion of the oil transporting pipe lines, pumps, valves and other involved equipments and also the refinery installations.

Commercial corrosion inhibitors are unique mixtures that may contain surfactants, film enhancers, demulsifiers, or an oxygen scavenger in addition to inhibitor moiety.

The purpose of this work was to synthesise some sulphur containing organic compounds which are higher in boiling point, rich in electron density and higher molecular weight (such as compounds of thioamide series). Synthesised thioamides were supposed to be evaluated regarding their anticorrosive properties in the artificial corrosive environment, similar to the formation water, in order to locate the suitable compounds which can compete with the preparations already available in the market for such purpose.

PREPARATION

The synthesis of thioamides are based on the Willgerodt Reaction [4–9]. The reaction is carried out by adding suitable amine in the mixture of sulphur and suitable ketone, in equimolar proportion. Thioamides result in the reaction of enamine with sulphur at 20°C. Enamine is generated at elevated temperature by the reaction of ketone and amine. The following is the general reaction model:

$$\underset{\text{Ketone}}{\mathrm{ArCOCH_2.R}} + \underset{\text{Amine}}{\mathrm{HNR_1R_2}} \xrightleftharpoons{130^\circ C} \underset{\text{Enamine 1}}{\mathrm{ArC(NR_1R_2)=CH.R}}$$

Where R = H or organic group
R_1 = H or organic group
R_2 = H or organic group

Then reaction of elemental sulphur with enamine results the isomerisation and thiolysis. This reaction is very fast and takes place favourably even at 20°C, as shown below:

$$\mathrm{Ar-\underset{\displaystyle NR_1R_2}{\underset{|}{C}}=CH.R} \xrightleftharpoons[S_8/20^\circ C]{\text{Isomerisation}} \mathrm{ArCH_2\underset{\displaystyle NR_1R_2}{\underset{|}{C}}=CH_2} \xrightleftharpoons[20^\circ C]{S_8} \mathrm{[ArCH_2\underset{\displaystyle NR_1R_2}{\underset{|}{C}}=CHSH]}$$

$$\xrightarrow[\text{stabilisation}]{\text{Irreversible}} \mathrm{[ArCH_2-\underset{\displaystyle N^+R_1R_2}{\underset{\backslash}{CH}}-\overset{\displaystyle H}{\overset{|}{C}}-S- \longrightarrow ArCH_2-CH_2-\underset{\displaystyle NR_1R_2}{\underset{|}{C}}=S}$$

EXPERIMENTAL PROCEDURE

A 0.2 Mole of amine was added to a mixture of 0.2 mole of ketone and 0.2 mole of sulphur at ambient temperature (21–24°C) in a heat resistant reaction flask. The flask was immediately connected with reflux condenser. The temperature of the flask was then gradually raised to 95–100°C, by controlled heating. The reaction mass was kept at this temperature with constant stirring for 4–5 hours. After elapsing the reaction time, the flask was allowed to cool. The reaction mass was dissolved in xylene in order to remove any unreacted sulphur. After evaporation of xylene the crystalline products were purified by recrystallisation in ethanol. The liquid products were not purified due to unavailability of very low vacuum facilities for complete removal of benzene. So crystalline products in purified form and liquid products in crude form were used for evaluation of anticorrosive properties of the synthesised compounds to screen out the effective compounds. The melting point of the crystalline products were measured and are mentioned in Table 1. The boiling point of the crude liquid products were not measured as the compounds contain xylene. The purification of these compounds will be done after the availability of the required vacuum facilities. The yield of crystalline products were calculated and given in Table 1. The yield of liquid products were not estimated due to impureness of the compounds.

Table 1. Experimental Yield of Crystalline Products

Compound code	m.p. in °C	Percent yield
iii	122–123	8.1
xii	96–97	47.3
xxi	129–130	59.4
xxii	74–75	85.3
xxiv	77–78	82.9

ANALYTICAL CHARACTERISATION OF THIOAMIDES

Study of I.R. Spectra

I.R. absorption bands of thioamides fall in the "Finger print" region of the spectra and are difficult to trace out normally [1, 10]. Secondly the vibrations of the $-CSN=$ group are not clearly seen due to strong coupling with other vibrations of the molecules. Strong absorption bands were found in the I.R. Spectra of the synthesised compounds. They were in the region of 700–850 cm^{-1}, 700–800 cm^{-1}, and in the region of 850–1000 cm^{-1}, for the primary, secondary and tertiary thioamides respectively. These bands indicate the presence of $=N-C=S$ (double bond) group in the compound under analysis. The above mentioned regions are the absorption regions of $N=C-S$ (single bond) group also.

Strong absorption bands in the region of 1300–1400 cm^{-1} in case of primary, secondary and tertiary thioamide, in I.R. spectras of the synthesised compounds are due to presence of $C-C$ and $C-N$ (single bond), which are also the absorption region of $C=N$ (double bond).

The above mentioned observation supports the concept of resonance stabilised planar $S-C-N$ skeleton of the thioamide molecules.

$$S-C=N \longleftrightarrow S=C-N$$

The absorption bands in the I.R. spectra of the synthesised compounds, in the region 1200–1300 cm^{-1} in case of primary thioamide, in the region 950–1150 cm^{-1} in case of secondary thioamide and in the region 1000–1200 cm^{-1} in case of tertiary thioamides, indicate the presence of $N-C-S$ group.

Strong absorption bands in the I.R. spectra of the synthesised compounds, in the region 1415–1480 cm^{-1} in case of primary thioamide, in the region 1525–1565 cm^{-1} in case of secondary thioamide and in the region 1490 to 1530 cm^{-1} in case of tertiary thioamide are due to the presence of $C-N$ and NR_2 groups.

The above observations confirm the presence of thioamide group in the synthesised compounds under investigation. I.R. spectra were obtained in KBr pellets by using PU-9512 IR spectrophotometer.

Ultraviolet Spectroscopic Evidence

$C=S$ group of thioamide has chromophoric properties. These compounds are bright yellow and yellowish brown in colour. The majority of their parent substances (ketones and amines) are colourless and few are white crystalline in nature. This interesting fact led to the identification of thioamide by UV/Vis Spectrophotometry. The UV/Vis spectra of the synthesised compounds were obtained, by using Milton Roy-1201 UV Spectrometer, in benzene. The results indicate that the synthesised compounds have characteristic long wavelengths, low intensity (R) band and the more intense (K) bands at shorter wavelength. This is in accordance with the behaviour of thioamides in these regions, as mentioned in the literature [1, 10]. According to Kasha's terminology (R) and (K) bands are due to the n-π^* and π to π^* transition respectively [10]. This classification is based on the MO calculations, polarised U.V. absorption spectra, solvent shifts, intensities and behaviour on protonation. The observed facts are given in Table 2.

Table 2, Ultraviolet and Visible Spectrophotometric Data of Synthesised Compounds

Compound code	λ_{max}(nm)	log ε
i	251.6	4.507
ii	253.6	4.509
iii	253.6	4.509
iv	269.8	4.523
v	253.6	4.510
vi	257.6	4.515
vii	259.7	4.517
viii	251.6	4.505
ix	255.7	4.510
x	256.3	4.504
xi	257.7	4.515
xii	255.6	4.521
xiii	253.6	4.508
xiv	254.6	4.501
xv	255.6	4.511
xvi	251.6	4.506
xvii	257.6	4.513
xviii	256.4	4.503
xix	263.7	4.519
xx	253.6	4.510
xxi	255.3	4.521
xxii	254.4	4.509
xxiii	253.6	4.510
xxiv	253.6	4.510
xxv	261.7	4.519
xxvi	259.6	4.521
xxvii	258.9	4.503
xxviii	259.3	4.513
xxix	267.7	4.522
xxx	253.6	4.509

Solvent used is Benzene.

EVALUATION OF ANTICORROSIVE PROPERTIES OF THE SYNTHESISED COMPOUNDS

Anticorrosive properties are measured by applying the procedure mentioned in the ID 182 using persistent film technique, in order to separate the compounds having more than 50% metal protection properties [11]. The Oil (Sirtika crude) and Brine water (composed of 9.62% NaCl, 0.305% $CaCl_2$, 0.186% $MgCl_2.6H_2O$ and 89.89% distilled water) were used in all the experiments. The Oil brine water ratio was chosen 10:90 (Oil-to-Brine water) and chemical (test compound) concentration based on the total volume of mixture of oil and brine was chosen 1%. Xylene was used as solvent for dissolution of test compounds. Prepolished carbon steel coupons were used throughout the experiment as test metal. The used coupons have available surface area equal to 13.2098×10^{-4} m^2 each. The procedure mentioned in the ASTM Designation G1-88 for preparing, cleaning, and evaluating corrosion test specimens was adopted in this work [12]. The anticorrosive test was carried out at ambient temperature for 72 hours and wheel speed was kept at 6 r.p.m. Table 3 shows the experimental results of test compounds in percentage protection and weight loss of the test coupons.

Anticorrosive properties of few of the mentioned compounds and the compounds commercially available as crude oil corrosion inhibitors in the concentration ranges from 10 to 100 ppm are measured in Brine water as well as in Sea water by using standard NACE Wheel Test method. The test conditions for all the above experiments are given in Table 4. Schematic diagram of the gas purging system and gas blanket assembly, used in the test experiments is illustrated in Fig. 1.

As this study was only limited to screen out the effective anticorrosive compounds from the synthesised products, the additives like surfactants, film enhancer etc. were not incorporated with the test compounds during the evaluation.

RESULTS AND DISCUSSION

Corrosion processes both anodic and cathodic are described in detail in the literature [2–3].

The effect of hydrogen sulphide is thought to be responsible for the acceleration of corrosion of iron. But in the presence of inhibitors such as amines, quaternary ammonium cations, thiourea, synergistic enhancement of inhibition is observed due to interaction of adsorbed HS^- ion with the adsorbed inhibitor.

The mechanism of action of organic corrosion inhibitors, depends on many factors, such as concentration; the pH of the corrosive environment; the nature of the anion of acid; the presence of other species in the corrosive medium; the extent of reaction to form secondary inhibitors and the nature of the metal. The activity of corrosion inhibitors, with the same functional group, may additionally vary with factors such as the effect of the molecular structure, electron density of the functional group and the size of the hydrocarbon portion of the molecule, unsaturations of the molecule and presence of electron rich elements [9].

Corroding metal surfaces in acid solution are oxide free, whereas in neutral solutions, the metal surfaces are covered with films of oxides, hydroxides or salts owing to reduced solubility of these species [9]. Inhibition in neutral solution is due to compounds which can form or stabilise protective surface films. The organic compounds containing sulphur inhibit the corrosion of metals in acid solution perhaps by donation of electrons from adsorbed molecules to the metal atoms or ions.

Sulphur containing compounds are considered to be superior in inhibition compared to nitrogen and oxygen containing compounds, as ionisation energy

Table 3. Effect of Synthesised Compounds on the Corrosion Properties of the Carbon Steel Coupons

Compound code	Percentage protection	Loss of wt. in g/m^2
BLANK	00.00	24.522
TH-i*	90.45	2.342
TH-ii	44.09	13.708
TH-iii*	88.78	2.751
TH-iv	40.73	14.535
TH-v*	58.14	10.264
TH-vi	21.05	19.360
TH-vii*	63.20	9.024
TH-viii*	75.84	5.924
TH-ix*	86.73	3.254
TH-x	21.62	19.220
TH-xi*	80.34	4.822
TH-xii*	87.57	3.048
TH-xiii*	64.04	8.817
TH-xiv	48.86	12.540
TH-xv*	55.90	10.815
TH-xvi	48.31	12.675
TH-xvii	44.66	13.570
TH-xviii	15.46	20.730
TH-xix*	83.88	3.953
TH-xx*	81.43	4.554
TH-xxi*	89.59	2.553
TH-xxii*	87.14	3.154
TH-xxiii	39.32	14.879
TH-xxiv*	89.18	2.653
TH-xxv*	84.69	3.754
TH-xxvi	21.06	19.357
TH-xxvii	13.75	21.150
TH-xxviii	86.33	3.352
TH-xxix*	87.14	3.154

*Compounds having percentage protection more than 50%.

Table 4. Test Conditions Used in All Performed Experiments

Test method	Temp. °C	Time (hrs)	CO_2 solubility at R. Temp. g/l	O_2 solubility at R. Temp. g/l	Crude oil (v/v) %	Brine water (v/v) %	Sea water (v/v) %
Wheel test method	25	72	1.5	0.001	10	90	—
Wheel test method	25	72	1.5	0.001	10	—	90

of sulphur is less than oxygen and nitrogen. These compounds attach themselves at the points which suffer anodic attack preferentially and they form a protective film on the metal by making co-ordinate covalent type of linkage with the metal atoms and by london forces. At anodic points, the inhibitor increases the electron atmosphere and render more difficult the detachment of positive metallic ions.

The inhibition of sulphur compounds is made more effective by introducing cyclic or aromatic group into the compounds. This not only increases the surface area of the molecule, but makes the sulphur more nucleophilic. The other groups which increase the nucleophilicity of the molecule of these compounds, when introduced into its molecules, increase the effectiveness of the compounds, regarding its anticorrosive activity. Shielding effect of organic inhibitors depends on the position of side chain [3]. The molecules having side chain at para position are more effective than the molecules having substitution at ortho and meta positions.

The effect of synthesised thioamides on the corrosion properties of steel coupons is given in Table 3. The test conditions for all the corrosion evaluation experiments are given in Table 4. List of synthesised compounds and their percentage composition of sulphur and nitrogen is given in Table 5. The solubility data of the synthesised thioamides in benzene, xylene,

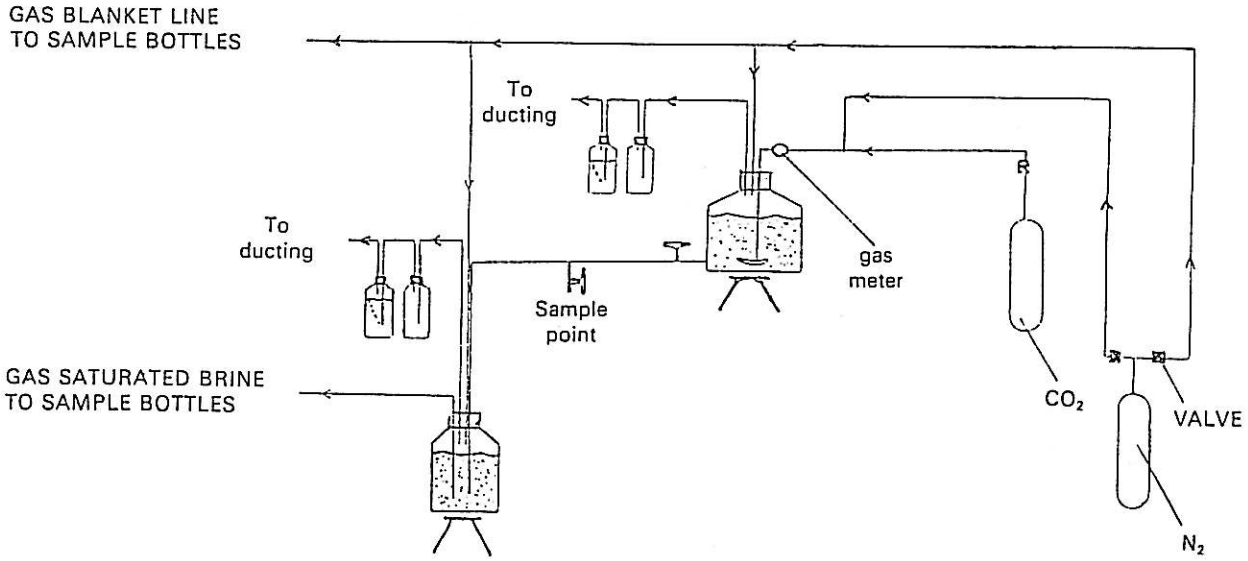


FIG. 1. Schematic diagram of the gas purging system and gas blanketing assembly used in the test experiments.

Table 5. List of the Synthesised Compounds and their Elemental Composition

Compound code	Formula	Percentage composition of S & N w/w			
		Calculated		Found	
		N	S	N	S
TH-i	CaHbNS	2.8	6.4	2.6	6.2
TH-ii	CaHbNS	4.3	9.7	4.1	9.6
TH-iii	CaHbNS	4.3	19.6	4.1	19.4
TH-iv	CaHbNS	4.4	10.1	4.6	10.3
TH-v	CaHbNS	4.4	10.2	4.3	10.1
TH-vi	CaHbNS	4.8	11.0	4.7	10.9
TH-vii	CaHbNS	5.0	11.5	4.9	11.4
TH-viii	CaHbNcS	10.4	11.8	10.5	11.9
TH-ix	CaHbNS	5.3	12.2	5.2	12.1
TH-x	CaHbNS	5.3	12.2	5.2	12.1
TH-xi	CaHbNcS	6.2	10.9	6.1	10.8
TH-xii	CaHbNS	5.5	12.6	5.6	12.7
TH-xiii	CaHbNcSO	7.9	11.1	8.0	11.3
TH-xiv	CaHbNcS	16.7	12.7	16.6	12.6
TH-xv	CaHbNcS	11.2	12.8	11.1	12.6
TH-xvi	CaHbNcSO	11.8	13.4	11.9	13.5
TH-xvii	CaHbNcS	17.7	13.5	17.5	13.4
TH-xviii	CaHbNcS	11.9	13.6	11.7	13.4
TH-xix	CaHbNS	5.9	13.6	5.7	13.4
TH-xx	CaHbNS	6.0	13.7	5.8	13.5
TH-xxi	CaHbNS	6.2	14.1	6.1	14.0
TH-xxii	CaHbNSO	6.3	14.5	6.3	14.4
TH-xxiii	CaHbNS	6.3	14.5	6.2	14.4
TH-xxiv	CaHbNS	6.4	14.6	6.2	14.4
RH-xxv	CaHbNS	6.8	15.4	6.7	15.3
TH-xxvi	CaHbNS	6.8	15.4	6.6	15.2
TH-xxvii	CcHbNS	6.8	15.6	6.7	15.5
TH-xxviii	CaHbNS	7.6	16.9	7.4	16.8
TH-xxix	CaHbNS	7.3	16.8	7.2	16.7

Note: In the above compounds the *a*, *b* and *c* are in the following range:

$a = 11$ to 33
$b = 13$ to 60
$c = 2$ to 3

kerosene, methanol and brine are indicated in Table 6. Heat stability data of these compounds in brine water is given in Table 6.

Schematic diagram of the gas purging system and gas blanketing assembly, used in the test experiments, are illustrated in Fig. 1. Corrosion protection properties versus concentration of inhibitor, of few of the synthesised compounds and some of the commercially available crude oil corrosion inhibitors, in the concentration range 10 to 100 ppm, using NACE Wheel Test method are illustrated in Figs. [2–5] respectively. From the results it appears that synthesised compounds show good inhibition when used in low concentration, but inhibition properties decrease at higher concentration. The increase in corrosion rate at higher concentration, in case of synthesised thioamides, may be due to the presence of effective amount of corrosion supporting organic species along with desired inhibitor molecules, as we have not purified our reaction products. The crude form of synthesised compounds were used in evaluation experiments to screen out the passive compounds. The Comparative studies show that the synthesised compounds are good anticorrosive preparations.

All the evaluation experiments are performed on laboratory scale. The results need reevaluation regarding the behaviour of pure form of synthesised thioamides under high pressure, high temperature, in the presence of CO_2 and H_2S as well as in the above mentioned experimental conditions. This will enable to choose the compounds having linear relationship

Table 6. Solubility and Stability Data of Synthesised Compounds in Common Organic Solvents and in Brine Water

Comp. code	Solubility in					Stability in		
	Benz.	Methanol	Xylene	Keros.	Brine	Cold 20°C	Hot 100°C	Brine
TH-i	+++	+++	+++	+++	− − −	St.	St.	St.
TH-ii	+++	+++	+++	++	− − −	Unst.	Unst.	St.
TH-iii	+++	+++	+++	+++	− − −	St.	St.	St.
TH-iv	+++	+++	+++	+++	− − −	Unst.	Unst.	St.
TH-v	+++	− − −	+++	++	− − −	St.	Unst.	St.
TH-vi	+++	++	+++	+++	− − −	St.	St.	St.
TH-vii	+++	+++	+++	+++	− − −	Unst.	Unst.	St.
TH-viii	+++	++	++	++	− − −	St.	St.	St.
TH-ix	+++	+++	+++	+++	− − −	St.	St.	St.
TH-x	+++	+++	+++	+++	− − −	St.	St.	WPPT
TH-xi	++	+++	++	++	− − −	Unst.	Unst.	St.
TH-xii	+++	+++	+++	+++	− − −	St.	St.	St.
TH-xiii	+++	++	++	− − −	− − −	St.	St.	St.
TH-xiv	++	+++	++	++	− − −	St.	Unst.	PPT
TH-xv	+++	++	++	+++	− − −	St.	Unst.	PPT
TH-xvi	++	++	++	++	− − −	Unst.	Unst.	PPT
TH-xvii	+++	+++	++	++	− − −	St.	St.	St.
TH-xviii	+++	+++	+++	++	− − −	St.	Unst.	St.
TH-xix	+++	+++	+++	+++	− − −	St.	St.	St.
TH-xxi	+++	+++	+	− − −	− − −	St.	St.	St.
TH-xxii	+++	+++	+++	+++	− − −	St.	St.	St.
TH-xxiii	+++	+++	+++	+++	− − −	St.	St.	St.
TH-xxiv	+++	+++	+	++	− − −	St.	St.	PPT
TH-xxv	+++	+++	+++	− − −	− − −	St.	St.	St.
TH-xxvi	++	+++	++	− − −	− − −	St.	St.	St.
Th-xxvii	+++	+++	+++	+++	− − −	Unst.	Unst.	St.
TH-xxviii	+++	+++	+++	+++	− − −	St.	St.	St.
TH-xxix	+++	+++	+++	− − −	− − −	St.	St.	St.
TH-xxx	+++	+++	+++	+++	− − −	St.	St.	St.

Note:

+++ = Completely soluble
++ = Soluble with difficulty, not completely
+ = Partially soluble and partly forming susp.
− − − = Very little soluble.
St. = Stable
Unst. = Unstable
PPT = Decomposition of the compound (Precipitation of sulphur)
WPPT = Decomposition of the compound (White precipitate appeared)

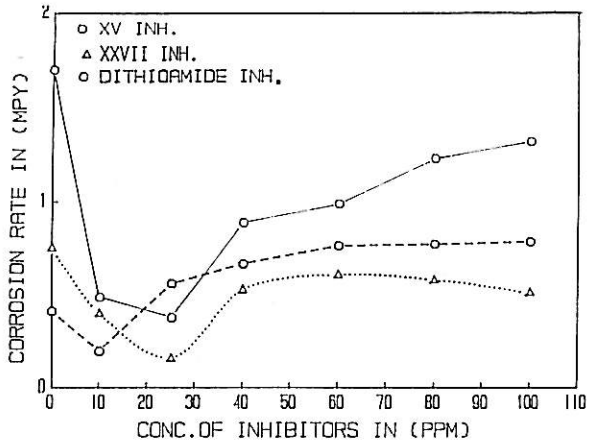


FIG. 2. Comparison of corrosion rate of different synthesized thioamides in brine water, at pH 4.5 to 4.8, in concentration ranges from 10 to 100 ppm, by using NACE standard wheel test method.

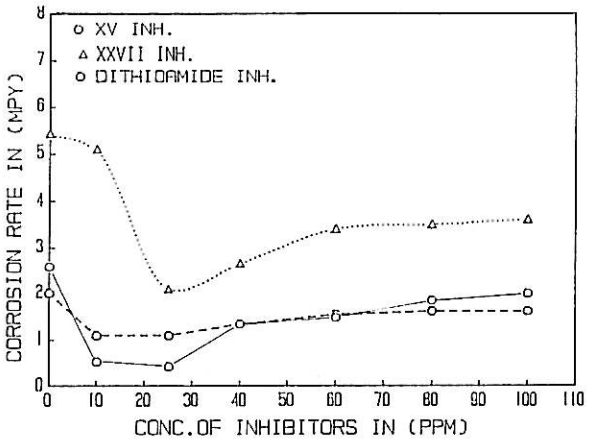


FIG. 3. Comparison of corrosion rate of different synthesized thioamides in sea water, at pH 4.5 to 4.8, in concentration ranges from 10 to 100 ppm, by using NACE standard wheel test method.

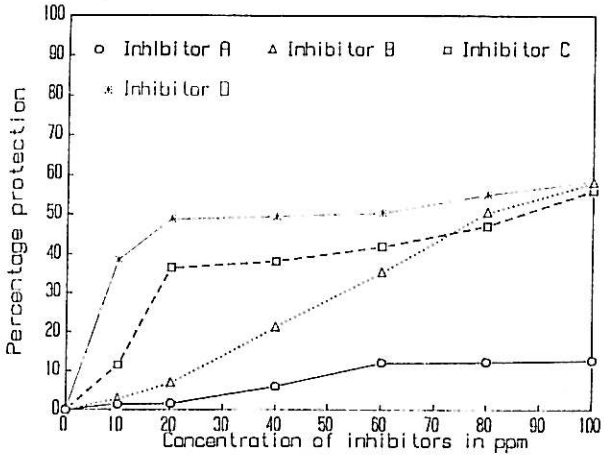


FIG. 4. Comparison of percentage protection of different commercially available amine base crude oil corrosion inhibitors, in brine water, at pH 4.5 to 4.8, in the concentration ranges from 10 to 100 ppm, by using NACE standard wheel test method.

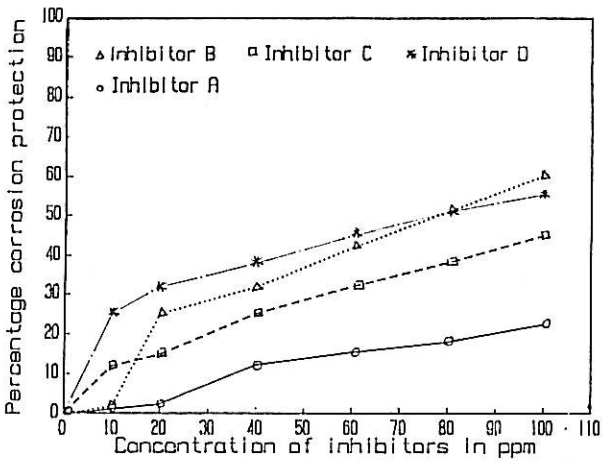


FIG. 5. Comparison of percentage protection of different commercially available amine base crude oil corrosion inhibitors, in sea water, at pH 4.5 to 4.8, in the concentration ranges from 10 to 100 ppm, by using NACE standard wheel test method.

between the corrosion rate and their concentration. Beside the above mentioned parameters it is also necessary to find out the emulsion tendencies and solubility percentage in the aqueous and oily medium in order to locate, in case of success, the suitable oil field application for the synthesised formulations.

CONCLUSION

In this work work series of thioamides different in molecular weight, molecular structure and molecular saturation, have been synthesised successfully. Their chemical characterisation and evaluation of anticorrosive properties, in crude form, are made in the artificial environment, similar to the formation water. Out of the synthesised compounds eighteen compounds were found to have percentage protection above fifty percent in the above specified environment. Comparative studies regarding the corrosion protection properties, of few of the synthesised and commercially available corrosion inhibitors show that the synthesised compounds are also good anticorrosives.

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