

Preparation of new saturated polyamide compounds and its application as corrosion inhibitors for corrosion of carbon steel in hydrochloric acid solution

New one series of saturated polyamide was prepared by polycondensation of methylenedisalicylic acid (MDSA) with adipic acid and several diamine such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine and pentaethylenehexamine. The structure of the prepared polyamide was detected by IR and ¹H NMR spectra physical properties of these compounds were detected. These compounds were tested as a corrosion inhibitors for dissolution of carbon steel type (L-52) used in Egyptian petroleum pipe lines in 0.1M HCl solution using potentiodynamic polarization technique. The percentage inhibition efficiency increases with increasing the inhibitor concentration and number of amino group in the structure of polyamide. The inhibitive action of these compounds was explained in view of adsorption of these compounds on the surface of steel. The adsorption follows Langmuir adsorption process isotherm.

INTRODUCTION

Polyamides compounds are widely used in several industrial materials because of their excellent comprehensive performance. For instance, almost all polyamides present relatively high strength, good toughness, and abrasion resistance. Their peculiar crystal structure, which is controlled by the interchain hydrogen bonds between amide groups, provides polyamides with attractive physical properties. Hydrogen bonds play an important role not only in determining the crystal structure but also in the overall performance of polyamides. Therefore, those polyamides with long or short alkyl segments have attracted much attention in recent years [1 - 5]. Long alkyl segment aliphatic polyamide has a relative low hydrogen bond concentration and thus a low melting point. It also shows prominent impact properties, a low dielectric constant, and lower water affinity compared with other polyamides containing short alkyl segments [6 - 7].

Carbon steel is a common constructional material for many industrial units because of its low cost and excellent mechanical properties. However, it suffers attack in service particularly in oil and gas production system. Although corrosion inhibitors are the most effective flexible mean of corrosion control in oil and gas production systems, the selection and application of inhibitors are actually complicated because of the variable corrosive environments in these systems.

Many organic compounds containing oxygen, nitrogen and sulphur atom have been used as corrosion inhibitors for carbon steel in various aggressive environment [8-16]. The addition of high molecular weight organic compounds such as polymer to inhibit the corrosion of carbon steel has found wide application in many fields. It has been reported that these compounds possess high inhibition efficiencies for steel corrosion [17-22]. The inhibition process is attributed primarily to the adsorption of the polymer molecule.

The aim of this work is to study the effect of five new prepared polyamide compounds (I-V) as corrosion inhibitors for dissolution of carbon steel (L-52) which used in Egyptian petroleum pipes lines using potentiodynamic polarization technique.

MATERIALS

All compounds such as: salicylic acid, formaldehyde 30% (EL-Nasr Comp., Egypt), ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine pentaethylene hexamine (Fluka), adipic acid (Aldrich, Comp.). All compounds were pure grade and used without purification, all organic solvents used are pure and used directly.

EXPERIMENTAL

1.1. Preparation of Methylene-DI-Salicylic Acid (MDSA)

A mixture of 27.6 gm (0.2 mole) salicylic acid [23], 12.62 gm (0.13 mole) of 30% formaldehyde and 180 gm of 40% sulphuric acid was placed in 250 ml one neck quick-fit round bottomed flask and allowed

Address authors: Chemistry Department, Faculty of Science, Benha University, Benha, Egypt
drsamykh@yahoo.com & metwally552@hotmail.com

to reflux for 8hr. The reaction mixture was cooled and filtered using buchner funnel, washed several times with cold water and finally with hot water to remove sulphuric acid and salicylic acid then dried at 110 °C for 8 hrs. The yield obtained about 92%, melting point 236-238 °C.

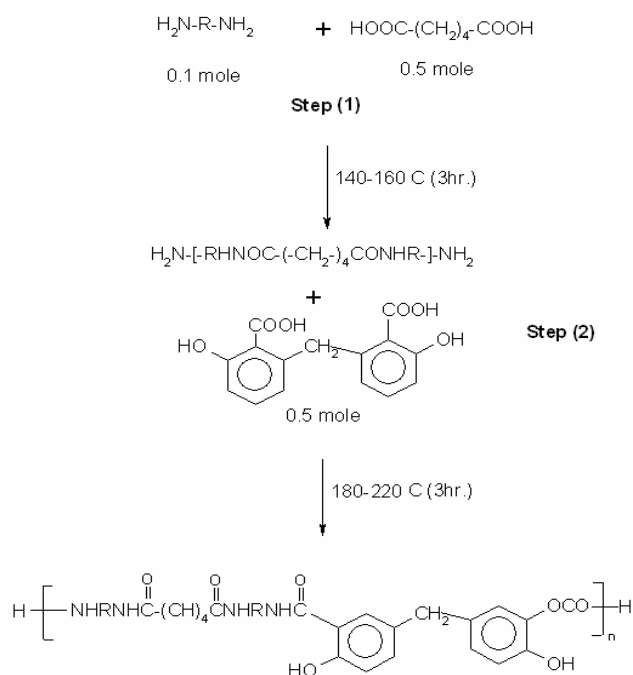
1.2. Preparation of Polyamide

Polyamides were prepared by two steps. The first step is reacting diamine with adibic acid at 140-160 °C and the second step is reacting the product with methylene disalicylic acid at 180-220 °C in reaction flask dipped in an oil bath (thermostatically controlled) provided with mechanical stirrer and Dean-

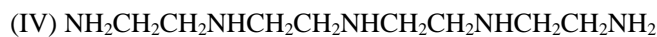
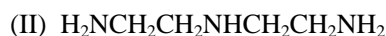
Stark stream of dry nitrogen insert in the flask to facilitate the removal of water.

At the end of the reaction the copolymers were purified by dissolving in DMF and precipitating into large amount of petroleum ether 40-60 for 6 hrs.

A reaction mixture containing (1 mol) of diamine, 73g (0.5 mol) of adibic acid (ADA) was stirred mechanically and heated to 140-160 °C. The temperature was raised gradually at interval time till the first step (3 hr.). The mixture was reheated in the second step from 180-220 °C, 144 g (0.5 mol) of methylene disalicylic acid (MDSA). The reaction was followed (Ca.3h). Then the product was cooled under nitrogen.



where: R



Scheme of copolymerization

1.3. Determination of Acid Value (AV)

The weighted sample of copolymer is placed in conical flask dissolved in DMF and titrated with (0.05 N) alcoholic KOH using phenolphthaline indicator till the endpoint and calculate AV according to the equation:

$$\text{AV} = \frac{N \times V \times 56.11}{\text{weight of sample}} \quad (1)$$

where:

N: the normality of KOH

V: the volume of KOH

1.4. Determination of Hydroxyl Value

3 gm of sample is placed in erlenmeyer flask and exactly 20 ml of acetylating mixture (1 volume of acetic anhydride 3 volume of pyridine) were reflux for 30 min. A blank determination is carried out at the same time. The flask was cooled by cold distilled water (50 ml) and the free acetic acid titrated with 1N NaOH then the hydroxyl value calculated by the standard methods [24].

1.5. Viscosity Measurements

The viscosities were determined by Ostwald[25] viscometer at six different concentrations ranged from 0.5 to 3.0% of the copolymer in DMF at 33 °C. The intrinsic viscosity (η) was calculated using Huggins equation [eq. (1)] and Krammer equation [eq. (2)]

$$\eta_{sp}/C = [\eta] + k_1[\eta]^2C \quad (2)$$

$$\ln \eta_{rel}/C = [\eta] - k_2 [\eta]^2C \quad (3)$$

where C is the concentration (g/100 ml), η_{rel} is the ratio of the viscosity of the solution (η) to the viscosity of the solvent (η_o) ($\eta_{rel} = \eta/\eta_o$) and η_{sp} is a function derived from η_{rel} . The relative viscosity ($\eta_{sp} = \eta - \eta_o/\eta_o = \eta/\eta_o - 1 = (\eta_{rel}) - 1$). k_1 and k_2 are constants for a given polymer / solvent temperature system.

1.5.1. Infrared Spectra

The infrared spectra were recorded by a Beckman 4220 infrared spectrophotometer in the range 400-4000 cm^{-1} .

1.5.2. Nuclear Magnetic Resonance Spectra

The proton magnetic resonance spectra (in DMSO-d₆ as a solvent and using TMS as a zero reference) were obtained at room temperature with a varian EM-390 spectrometer operating at 200 MHz.

1.5.3. Potentiodynamic Polarization Measurements

The weight composition of the carbon steel (L-52) is the following 0.26%C, 1.35% Mn, 0.04%P, 0.05%S, 0.05%Nb, 0.02%V, 0.03%Ti, and the remainder is iron. A cylindrical rods embedded in araldite with an exposed surface area of 0.78 cm^2 . Before each experimental, the electrode was polished with different grade emery papers, degreased with acetone, rinsed under running water and finally dried between two filter paper.

The potentiodynamic polarization was performed at a scanning rate of 10 mV/sec using PG₃ Gamry Potentiostat. The current density potential curves recorded on 105DC corrosion software. The potentials were measured relative to a saturate calomel electrode (SCE) and the electrolytic cell was all pyrex and is described elsewhere [26].

The inhibition efficiency (IE) was calculated using the following equation:

$$IE = \left[1 - \frac{I_{corr.add}}{I_{corr.free}} \right] 100 \quad (4)$$

where, $I_{corr.add}$ and $I_{corr.free}$ are the corrosion current density in presence and absence of inhibitors.

RESULTS AND DISCUSSION

The structure of the prepared monomer (MDSA) and polyamide were confirmed by IR, ¹H NMR spectra. In IR spectra of (MDSA) show abroad band at 3300-3500 cm^{-1} ν_{OH} of carboxylic and phenolic, strong band at 2850 ν_{CH} aliphatic, band at 1690, 1610 $\nu_{C=O}$, $\nu_{C=C}$ aromatic ring, bands at 1430, 1210 ν_{C-O} , $\nu_{C=C}$, aromatic ring, bands at 1430, 1210 ν_{C-O} , ν_{CH} , bands at 790 cm^{-1} stretching vibration of substituted benzene. The ¹H NMR of (MDSA) show bands at δ 3-8 (2H) Ar-CH₂-Ar, (6H) Ar with interference at δ 6.8-7.8 and δ 11.58 (2H) COOH.

The IR spectra of polyamide as example (compounds II & III) show sharp band at 3340 ν_{NH} bands at 305, 2960 ν_{CH} aromatic and aliphatic bands at 1650, 1520 ν_{CONH} amide link bands at 1605, 1430 $\nu_{C=C}$ aromatic, ν_{C-O} bands at 785 stretching vibration of substituted benzene.

The ¹H NMR of polyamide were studied and used to both qualitative and quantitative analysis of polyamide by using method of Baddar et al.[27] as shown in Table (1) which indicate. The percent between the two monomers diacide and diamine in the prepared polyamide almost 50/50%. Which confirm that the stoichiometric calculated amounts of monomers polymerize to give alternating to polyamide with exactly medium Mwt.

The physical properties of the prepared saturated polyamide were determined in Table (2). The determination of hydroxyl value (OHV) and acid value (AV) and by means of these values as analysis to calculate the average molecular weight (Mwt.) of the product polyamide which used to determine the degree of polymerization. From these values we can say that the structure of the polyamide take the form of alternating copolymer include medium Mwt and have polar group in the polymer chain. The determination of acid value at interval of time and temperature to operate the preparation process and confirm that all components in the reaction mixture polymerize to give high degree of repeating units. The solubility of the prepared copolyamide are listed in Table (3) which indicated the solubility of these polyamides

were determined for the samples in excess solvents. All the polyamides are readily soluble in common polar a protic solvents on cold and heating with different solvents such as methyl, ethylalcohol. The

good solubility behavior of most of the prepared polyamides can be explained by the lower interaction between the chains.

Table (1): ¹H NMR spectral data of unsaturated polyamide (I-VIII)

Polymer	Component	Chemical shift δ (ppm)	No. of proton	Assignment	Peak area integration	Relative mole amount	Mole %
I	*Acid	6.9-7.1, 7.5, 1.4, 3.7, 3.75, 3.85	18	6(H)Ar,(4H) 2(CH ₂), (4H)2CH ₂ CONH (2H)CH ₂ -Ar, (2H)2(OH)	50.94	2.83	49.389
	**Amine	2.92, 3.09	12	8H 4(CH ₂),(4H)4(NHCO)	34.8	2.9	50.610
II	Acid	6.8-7.07, 1.4, 3.01, 3.48, 3.83	18	(6H)Ar, (4H) 2CH ₂ , (4H)2 CHCONH(2H) CH ₂ -Ar(2H) Ar-OH	46.26	2.57	51.093
	Amine	2.7, 3.09, 7.9-8.7	22	(16H), (H) 8CH ₂ -NH, (2H) NHCH ₂ , (4H)NHCO	54.12	2.46	48.906
III	Acid	6.9-7.4, 1.45, 3.26, 3.62, 6.6	18	6(H) Ar, (4H) 2CH ₂ -(4H) ₂ CH ₂ CONH (2H)CH ₂ -Ar(2H)HO-ArO	32.94	1.83	51.111
	Amine	3.26-3.46, 7.9, 8.2	32	(4N)18CH ₂ NH, (4H)4NHC(4H)4NH-CO	56.00	1.75	48.888
IV	Acid	6.94-7.32, 1.47, 3.7, 3.75, 3.83	18	(6H) Ar, (4H)2CH ₂ -C(4H)2CH ₂ CO-NH(2H)CH ₂ -Ar, (2H)2(OH)	60.66	3.37	50.373
	Amine	3.1-3.4, 8.2-8.64	44	(32H) 16CH ₂ NH (8H)8NH-CH ₂ -(4H)4NHCO	146.08	3.32	49.626
V	Acid	6.82-7.3, 1.49, 3.6, 3.7, 3.6, 3.8	18	(6H) Ar, (4H)2CH ₂ -C(4H)2CH ₂ CO-NH(2H)CH ₂ -Ar, (2H)2(OH)	34.92	1.94	50.339
	Amine	2.9-3.1, 3.66, 3.8,	52	(40H) 20CH ₂ NH, (8H)8NH-CH ₂ -(4H)4NHCO	99.32	1.91	49.610

*Acid: ADA, MDSA

** Amine: Diamine

Table (2): Physical properties of saturated copolyamide

Polymer	Nature	Yield	Acid value	Hydroxyl value	Mean Mwt	n*	Viscosity(η) d/L
I	Viscous	93%	24.34	49.75	1052.5	21.65	0.987
II	//	95%	22.1	65.21	13565.9	23.15	0.923
III	//	88%	30.46	46.68	15563.08	22.49	0.745
IV	//	91%	27.83	44.58	18336.02	24.19	0.551
V	//	94%	32.19%	48.13%	16322.96	19.34	0.431

n: Degree of polymerization

Table (3): Solubility of copolyamide

Polymer	CH ₃ OH	C ₂ H ₅ OH	Acetone	DMF	DMSO	Conc. HCl	Conc. H ₂ SO ₄	10% NaOH
I	+	+	-	++	++	+	+	+
II	+	+	-	++	++	+	+	+
III	+	+	-	++	++	+	+	+
IV	+	+	-	++	++	+	+	+
V	+	+	-	++	++	+	+	+

++ = Soluble in cold, + = Soluble after heating, \pm = Partially soluble, - = Insoluble

Fig. (1) show the relation of acid values and time the reaction with gradually increasing temperature all over the time of polymerization, which show the continuous decrease of a cid value with increasing of temperature and time of polymerization. This decre-

se of acid value indicates the consumer acid link and increase amide link. This led to increase the polyamide molecular weight and give more stable polyamide in different pH value.

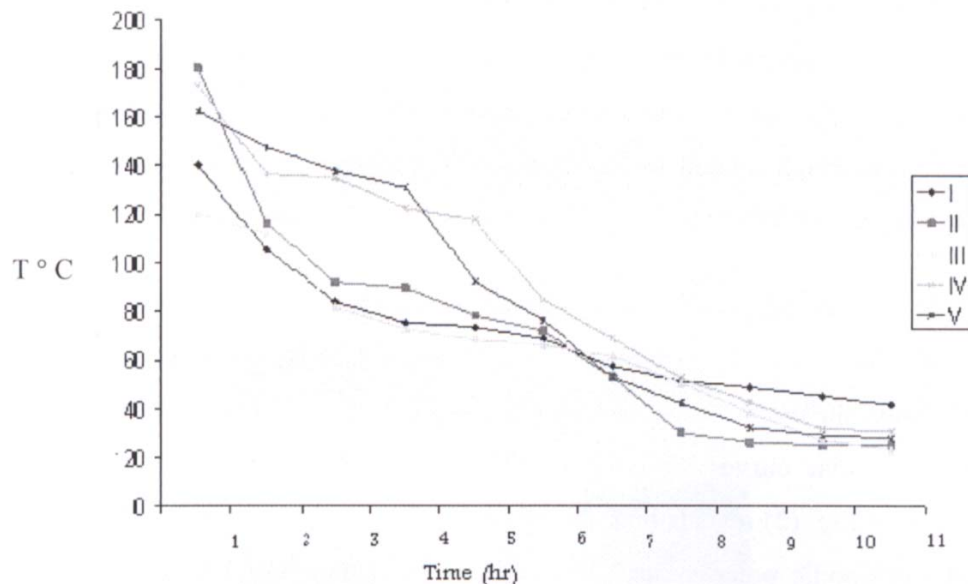


Fig. (1): Time-temperature program in the polycondensation of copolyamide (I-V)

Viscometric measurements were carried out in a DMF with Ostwald viscometer [25]. The reduced viscosity (η_{red}) versus the concentration (0.5-3.0%) was plotted for the set of data. (η) was determined from corresponding linear plots. Equation (1) and (2) were used to determine the Huggin and Krammer constants, respectively. As η_{red} is dependent on the concentration of the polymer sample, it is necessary to extrapolate a plot of η_{red} against the polymer concentration (C) to the zero concentration to get $[\eta]$, which is characteristic parameter of a polymer. Hence $[\eta]$ is given in equations (5) and (6) as follows:

$$[\eta] = (\eta_{sp}/C)C \rightarrow 0 \quad (5)$$

or

$$[\eta] = (\ln \eta_{rel}/c) C \rightarrow 0 \quad (6)$$

According to this relation, the plots of η_{sp}/C and $\ln \eta_{rel}/C$ against C were linear with slopes of K_1 and K_2 , respectively. The intercept on the viscosity function axis gave the $[\eta]$ value in both plots. The calculated values of constants k_1 and k_2 satisfy the relation $k_1 + k_2 = 0.5$ favorably [28], and this indicates that the solvent used or the viscosity measurement was of good quality; $[\eta]$ for the polyamides were show in Table (2). The data of viscosity measurement show relative decrease from polymer II-V which related to the increase of hydrogen bond and also to use of aromatic amine.

The effect of addition of polyamide compounds on the potentiodynamic polarization curves of the carbon steel electrode in 0.1 M HCl solution was studied. Fig. (2) shows the effect of increasing concentrations of compound V as an example. However, similar curves were obtained for the other compounds (not shown). Inspection of Fig. (2) reveals that, there is a transition region at the beginning of the cathodic or anodic polarization known as pre-Tafel region []. This starts from the corrosion potential and extends to the beginning of the Tafel region. It is characterized by a simultaneous occurrence of cathodic hydrogen evolution reaction and dissolution of steel.

The presence of increasing concentrations of polyamide compounds cause a marked decrease in corrosion rate i.e. shifts the anodic curves to more positive potentials and the cathodic curves to more negative potentials. This may ascribed to adsorption of these compounds over the metal surface. The corrosion current density ($I_{corr.}$) was determined from the intersection of the linear part of cathodic and anodic curves with corrosion potential ($E_{corr.}$).

The corrosion parameters such as, corrosion potential ($E_{corr.}$), corrosion current density ($I_{corr.}$), cathodic (ba) and anodic (ba). Tafel slopes and inhibition efficiency (IE) were calculated and given in Table (4).

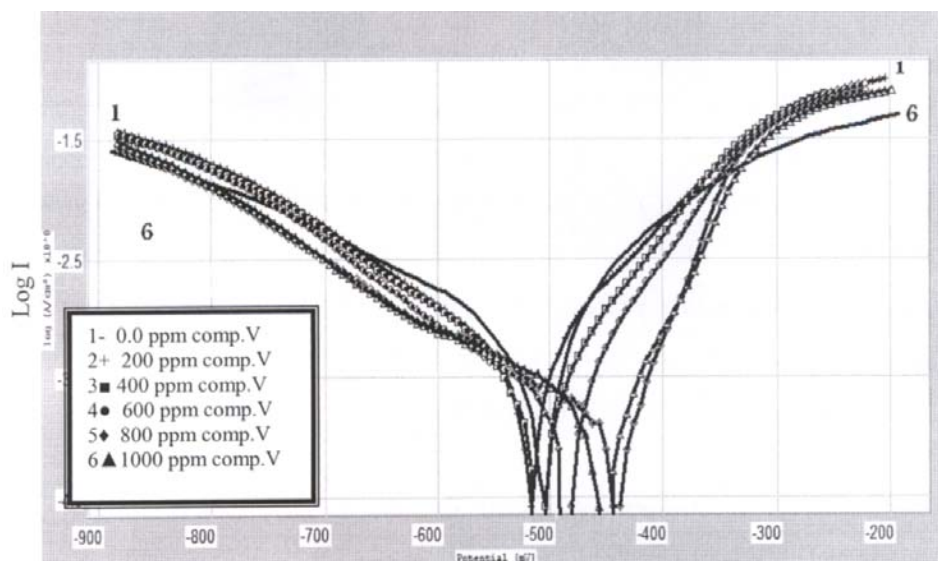


Fig.(2): Potentiodynamic polarization curves for carbon steel in 0.1 M HCl in absence and presence of different concentrations of compound (V) at a scan rate 10 mVs⁻¹

Table (4): Corrosion parameters of C-steel corrosion in 0.1 M HCl in the absence and presence of various concentrations of polyamide compounds as calculated from potentiodynamic polarization

Concentration	B _a mV/decade	-b _c mV/decade	-E _{corr.} mV (SCE)	I _{corr.} μA/cm ²	% I.E	θ
0.1M HCl + compound I						
0.00 ppm compound I	104	66	503	511	-	-
200 ppm compound I	108	68	500	301	41.09	0.411
400 ppm compound I	112	70	492	266	47.94	0.479
600 ppm compound I	116	72	485	205	59.88	0.599
800 ppm compound I	122	72	480	170	66.73	0.667
1000 ppm compound I	130	75	473	103	79.84	0.798
0.1M HCl + compound II						
200 ppm compound II	112	71	502	285	44.22	0.442
400 ppm compound II	121	73	496	226	55.77	0.558
600 ppm compound II	133	76	488	165	67.71	0.677
800 ppm compound II	148	80	482	105	79.45	0.795
1000 ppm compound II	148	82	475	88	82.77	0.828
0.1M HCl + compound III						
200 ppm compound III	115	70	506	279	45.40	0.454
400 ppm compound III	125	75	503	212	58.51	0.585
600 ppm compound III	130	78	495	114	77.69	0.777
800 ppm compound III	138	81	480	86	83.17	0.832
1000 ppm compound III	146	83	470	54	89.43	0.894
0.1M HCl + compound IV						
200 ppm compound IV	122	72	510	252	50.68	0.507
400 ppm compound IV	130	78	522	198	61.25	0.613
600 ppm compound IV	138	81	500	105	79.45	0.795
800 ppm compound IV	142	85	483	78	84.73	0.847
1000 ppm compound IV	148	89	460	40	92.17	0.922
0.1M HCl + compound V						
200 ppm compound V	120	73	515	215	57.92	0.579
400 ppm compound V	128	77	510	170	66.73	0.667
600 ppm compound V	135	83	484	100	80.43	0.804
800 ppm compound V	140	89	449	60	88.25	0.883
1000 ppm compound V	144	91	440	22	95.69	0.957

Inspection of the data cited in this table reveals that, as the concentration of the additives increases the corrosion potential (E_{corr}) is shifted to more noble direction, the corrosion current density (I_{corr}) decreases and the inhibition efficiency increases indicating the inhibiting effect of such compounds. These compounds act as mixed type inhibitors because they enhanced both the anodic and cathodic Tafel slopes. The inhibition efficiency of these compounds decreases in the following order:

$$\text{Compound V} > \text{IV} > \text{III} > \text{II} > \text{I}$$

ADSORPTION ISOTHERMS

Basic information on the interaction between the inhibitor and the steel surface can be provided by the adsorption isotherm. The polarization curves were analyzed to study the inhibition efficiency and mode of adsorption of the polyamide for corrosion of carbon steel in 0.1M HCl. The degree of surface coverage, θ of the metal surface was calculated from the following relation.

$$\theta = 1 - \frac{I_{\text{corr. add}}}{I_{\text{corr. free}}} \quad (7)$$

where, $I_{\text{corr.add}}$ and $I_{\text{corr.free}}$ are defined, previously. Attempts were made to fit the θ values to various isotherms including Langmuir, Temkin, Frumkin, Freundlich and Flory-Huggins. By far the best fit is obtained with the Langmuir isotherm. Langmuir adsorption isotherm was found to be the best description of the adsorption isotherms were assessed, Langmuir adsorption described by the following equation:

$$\frac{C}{\theta} = \frac{1}{k} + C \quad (8)$$

Where, C is the inhibitor concentration and K is the equilibrium constant of adsorption.

The plotting of C/θ against C gives a straight line with unit slope, Fig. (3). This indicate that the adsorption of the polyamide compounds on carbon steel surface is 0.1M HCl solution follows Langmuir's adsorption isotherm and consequently, there is no interaction between the molecules adsorbed at the metal surface.

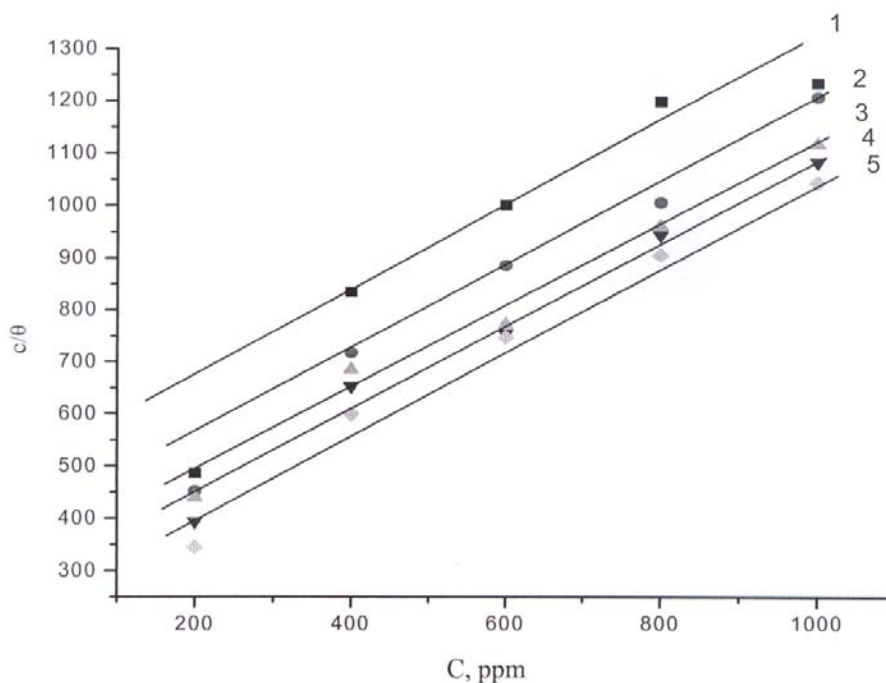


Fig. (3): Langmuir adsorption isotherm: (1) Compound I, (2) Compound II, (3) Compound III, (4) Compound IV, (5) Compound V

MECHANISM OF INHIBITION

The inhibition of corrosion of C-steel in hydrochloric acid by the investigated polyamide compounds as determined from potentiodynamic polarization was found to depend on the concentration, the nature of inhibitor, and the type of diamine in the polymer compounds. The observed corrosion data in the presence of polyamide compounds, decrease the value of corrosion current density and increase the values of θ and IE.

The observation indicates that the corrosion inhibition is due to the adsorption of the polyamide at the surface steel [30]. The nature of the inhibitor interaction on the metal surface during corrosion inhibition can be explained in terms of its adsorption characteristics [31]. The polyamide compounds contains different diamine units. As the number of diamine unit increases the values of IE increases the inhibitive effect of these compounds due to the presence of more than one amine groups in the chemical structure. This leads to horizontal adsorption of the polyamide compounds on the steel surface and isolate the metal from corrosive environments. Also, the values of IE increases with decrease the value, of viscosity as shown in Table (4). The protective efficiency increases with increase the diamine unit present in the molecule.

The adsorption of the polyamide molecule at the metal surface is usually through the already chloride ion. In acidic solutions, amines exists as cations and adsorb through electrostatic interaction between the positively charged amines cations and adsorbed chloride ions. The higher inhibitive properties with large molecular size which ensures greater coverage of the metallic surface.

REFERENCES

- [1] Jones NA., Coopers J., Atkins EDT., and Hill MJ., Francol, Temperature -induced changes in chain-folded lamellar crystals of aliphatic polyamides Investigation of Nylons 26,28,210 and 212, *J. of Polymer Sci.*, part b ; *Polymer Physics*, **35**(4), 675-688, 2003.
- [2] Pujgali J., and Subrirana J.A. Crystal structures of Nylon 56. A model with two hydrogen bond directions for Nylons Derived from add diamines, *Macromolecules*, **31** (24) 8540-8548 1998.
- [3] Franco L., Subirana J.A. and Buiggali J. Structure, and morphology of odd polyoxamides (Nylon 9,2). a new example of hydrogen, bonding interactions in two different directions, *Macromolecules*, **31** (R/2), 3912-3924 1998.
- [4] Murthy N. S., Curran S. A. Aharony S. M. and Minor H. Premelting crystalline relaxations and phase transitions Nylon 6 and 6.6, *Macromolecule*, **24** (11), 3215-3220 1991.
- [5] Yan D. Y., Li Y. J., and Zhu X. Y., Preparation, characterization and crystalline transition behaviors of polyamide 4/4 *Polymer*, **42**,5055, 2001.
- [6] Li; Y.J. Yan, D. Y., Brill transition in Nylon 10 12 investigated by variable temperature XRD and real time FT-IR *Macromol Rapid Commun.* **21**, 1282, 2000.
- [7] Yan; D.Y. Li; Y.J. Zhu, X, Y. Crystalline transition in Nylon 1010 *Macromol Rapid Commun.* **21** (2000) 1040.
- [8] Serhiri L., Yan D.Y. The effect of temperature on the corrosion of mild steel in acidic media in the presence of some sulphur containing organic compounds, *Mater Chem. & Phys.* **98**(2-3),316-323, 2006.
- [9] Abdel-Rehim S. S., Kaled K. F. and Abd El-Shafi N., S. Electrochemical frequency modulation as new technique for monitoring corrosion inhibitor of iron in acid media by new thiourea derivative. *Electrochim Acta*, **51**(16), 3269-3277 ,2006.
- [10] Alsabagh A. M., Migahed M. A. and Awad H. S. Reactivity of polyester aliphatic amine surfactants as corrosion inhibitors for carbon steel in formation water (*deep well water*) ,*Corros Sci*, **48** (4), 813-82,2006
- [11] Larabil, Hareky, Benolio, Ghalems, Hydrazide derivatives as corrosion inhibitors for mild steel in 1M HCL, *Progress in Organic Coatings*, **54** (3), 256-262, 2005.
- [12] Abdallah M, Corrosion behavior of 304 stainless steel in sulphuric acid solution and its inhibition by some substituted pyrazolone, *Mater. Chem. & Phys*, **82**, 786-792 ,2003.
- [13] Abdallah M., Helal E. A., Fouda A. S., Aminopyrimidine derivatives as inhibitors for corrosion of 1018 carbon steel in nitric acid solution, *Corros Sci*, **48**, 1639 -1654,2006.
- [14] Ozcan M., Dehri I., and Erbil M., Organic sulphur containing compounds, as corrosion inhibitors for mild steel in acidic media correlation between inhibition efficiency and chemical structure, *Appl. Surf. Sci*, **236** (1-4) 155-164, 2004
- [15] Selvi S., Ramon V., and Ajendran J., Corrosion inhibition of mild steel by benzotriazole derivatives in acidic medium , *J. of Appl. Electrochem.* **33** (12) 1175 -1182, 2003.
- [16] Kraljic M., Mandic Z. and Duic J. Inhibition of steel corrosion by polyaniline coating ,*Corros. Sc.*, **45** (1), 181-198, 2003.
- [17] Aramoki k., Shimura T., An ultrathin polymer coating of carboxylate self - assembled mono layer adsorbed on passivated iron to prevent iron corrosion in 0.1M Na₂SO₄, *Corros. Sci.*, **52**(1), 1-6, 2010.

- [18] Umoren SA., Edouk UM., Oguzie EE., Corrosion inhibition of mild steel in 1M H₂SO₄ by polyvinyl pyrrolidone and synergistic iodide additives, *Portug. Electrochim. Acta*, **26** (6), 533-546, 2008.
- [19] Chany G., Naik YA., Vijaykumar S., and Venkatesha T. V., Sherigare BS. An Electroactive copolymer as corrosion inhibitor for steel in sulphuric acid medium B. S, *Appl Surf. Sci.* **254** (17), 5569 – 5573, 2008.
- [20] Amin, MA, Abd El-Rehim ss, El- Sherbini EF, Hazazi OA, Abbas MN, Polyacrylic acid a corrosion inhibitor for aluminium in weakly alkaline solutions part: Weight loss, polarization impedance EFM and EDX studies, *Corros. Sci.*, **51**(3), 658- 667, 2009.
- [21] Finsgar M, Fassbender S., Nicolini F, Milosev I, Polyethyleneimine as corrosion inhibitor for ASTM 420 stainless steel in near – neutral saline media, *Corros. Sci.* **51** (3), 525- 533, 2009.
- [22] Parelekar M.H., Bhatt HA. and Potnis, SP., New intermediates for plastics & coatings: preparation and characterization of Methylene – D I- Salicylic – Acid, *Indian Chem. Soc.*, **49**, 1201-1207, 1972.
- [23] Manjusha M., Jadhao L., Bhave N.s, Resin IV, Synthesis, characterization, and Ion – Exchange Properties of a 2,2- Dihydroxy biphenyl Formaldehyde Copolymer Resin, *Journal of Applied Polymer Sci.*, **109**, 508 -514, 2008.
- [24] Abd El-Haleem S. M., Abd El-Fattah A. A., and Taylor W. Inhibition of pitting corrosion of zinc using some organic amines, *Res Mechanica*, **30**, 53, 1983.
- [25] Baddar, F. G. Nosseir M. H. Messiha N. N. and Ikladious N. E., Polyesters – part IV. Structural elucidation of phenylitaconic polyesters by joint application of I. R., U.V. and NMR spectroscopy, *Eur. Polym.j.*, **12**, 631, 1976.
- [26] Jadhao, M.M, Paliwal, LJ.; Bhave, N.S.J. Resin III: Synthesis characterization and ion Exchange Properties of 2,2-Dihydroxy biphenyl Urea-formaldehyde Ter-polymers., *Appl. Polym. Sci.* **96** 1605, 2005.
- [27] Abdallah M., Megahed H.E., El-Etre A Y., Obied M. A., and Mabrouk E.M. Polyamide compound as inhibitors for corrosion of aluminum in oxalic acid solutions. *Bull ElectroChem.* **20** (6), 277-281, 2004
- [28] Alsarawy A. A., Fouda A. S., Shehab El-Din W. A., Some Thiazole derivatives as corrosion inhibitors for carbon steel in acidic medium, *Desalination*, **229** (1-3), 279- 293, 2008.
- [29] Khaled K.F., Adsorption and inhibitive properties of new synthesized guanidine derivative as corrosion of copper in 0.5 M H₂SO₄ *Appl. Surf. Sci.* **255** (5), 1811-1818, 2008.