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#### International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Sayyah, S. M., El-Rehim, S. S. Abd and El-deeb, M. M.(2001) 'The Effect of Some Polymers on the Corrosion Behaviour of Tin in 1 M NaCl Solution', International Journal of Polymeric Materials, 49: 1, 59 — 80 To link to this Article: DOI: 10.1080/00914030108035867 URL: http://dx.doi.org/10.1080/00914030108035867

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## The Effect of Some Polymers on the Corrosion Behaviour of Tin in 1 M NaCl Solution

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(Received 25 December 1999; In final form 28 December 1999)

The effect of various concentrations (0.5 to 30 ppm) of polyacrylamide samples which have different molecular weights (sample  $A = 3.4 \times 10^4$ ,  $B = 1.52 \times 10^4$  and  $C = 1 \times 10^4 \text{ gmol}^{-1}$ ) and poly(propenoyl glycine) (sample D) which has the same degree of polymerization  $(D_p)$  of sample C on the corrosion behaviour of tin in 1 M NaCl solution were investigated at 20°C using potentiodynamic polarization technique. The various electrochemical parameters ( $I_{corr}$ ,  $R_{p}$ ,  $E_{pit}$  and  $I_p$ ) were calculated from Tafel plots in the absence and presence of these polymers. The data reveal that the inhibition efficiency of polymer C is higher than that of polymer B, while the presence of polymer A (the highest molecular weight) accelerates the corrosion of tin in 1 M NaCl indicating that the inhibition decreases with increasing molecular weight. On the other hand, polymer D shows the strongest inhibition efficiency. For the investigated polymer inhibitions B, C and D, it was found that the experimental data fit Flory-Huggins adsorption isotherm. The effect of temperature on various corrosion parameters and the inhibition efficiency was studied for polymer D (10 ppm) in 1 M NaCl over the temperature range from 20°C to 50°C.

Keywords: Polyacrylamide; Poly(propenoyl glycine); Tin; Corrosion

#### 1. INTRODUCTION

Tin is soft, ductile, malleable and has a relatively low melting point  $(231.9^{\circ}C)$ . It is easily solderable, so it is widely used in industry as

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a protective coating material for iron in contact with electrolyte solutions of divers compositions, and foodstuff [1], exhibiting of various phenomena of electrochemical corrosion [2-6]. To avoid corrosion attack, various chemical compounds are added to aggressive solutions such as nitric acid [7], hydrochloric acid [8], oxygen-free solutions of organic acids [9] and sodium chloride solution [10].

Recently, water soluble polymeric compounds attracted great interest as corrosion inhibitors for different metals in different media [11-22]. Polyacrylamide (PAA) was used as corrosion inhibitor for silver and titanium [11]. Girchev et al. [12] studied the adsorption of polyacrylic acid (PAAC) or polyacrylamide (PAA) on iron and gold by using cyclic valtammetry technique in  $H_2SO_4$  and both polymers were strongly adsorbed on iron and gold which means that they are good inhibitors for these metals in the investigated medium. Polyvinylpyrrolidone and polyethylenimine are used as corrosion inhibitor for metallic materials in acidic medium [13-19]. Polyvinylpyrrolidone has received particular attention and has been applied to the inhibition of Al in hydrochloric acid [20] and Fe in sulphuric acid [21]. Sekine et al. [22], studied the effect of cationic polymers and anionic polymers as corrosion inhibitors for mild steel in cooling water system instead of using chromate and other inorganic inhibitors due to environmental safety. Some vinyl polymers, polypectine and polycarboxy methylcellulose were investigated as corrosion inhibitors for iron electrodes in acid media [23]. Protection of heat exchange surface from calcium sulfate solutions was made by polyacrylic acid, polyaspartic acid and polyglutamic acid [24].

In view of these results, the present work was devoted to study the effect of polyacrylamide and poly(propenoyl glycine) on the corrosion behaviour of tin in 1 M NaCl solution.

#### 2. EXPERIMENTAL

#### 2.1. The Working Electrode

The working electrode employed in the present work was made from pure tin rod (99.9% Koch light laboratories, England) axially embedded in an araldite holder to offer an active flat disc shaped surface of an area 0.785 cm<sup>2</sup>. Prior to each experiment, the working electrode was polished successively with fine grade emery papers. The polished metal surface was rinsed with acetone and distilled water before dipping it into the electrolytic cell. A platinum wire was used as the counter electrode. A saturated calomel electrode (SCE) was used as a reference electrode to which all potentials are referred. For each run, a freshly prepared solution as well as a clean set of electrodes were used. Potentiodynamic polarization experiments were employed using a potentioscan type apparatus (Potentiostat/ Galvanostat EG and G 273 A). The experiments were carried out by changing the electrode potential automatically from the starting potential toward more positive values at the required scan rate till the end of the experiment. The E/I curves were recorded by computer software from the same company Model 352 and 270/250. All solutions were freshly prepared using doubly distilled water and analar chemicals.

#### 2.2. Polymer Inhibitors

#### 2.2.1. Polyacrylamide

Polyacrylamide was prepared by aqueous polymerization using sodium meta bisulphite (NaHSO<sub>3</sub>) as free radical initiator under nitrogen atmosphere at 40°C. In a well-stoppered conical flask of 250 ml capacity, the amount of initiator (0.01, 0.05 and 0.1 gmol/l respectively) in 100 ml distilled water followed by the amount of monomer (acrylamide) (one gram) was added to the reaction mixture under nitrogen atmosphere. The conical flasks were then put in an automatically controlled thermostatic water bath at 40°C. The flasks were shaken (15 shakings/10 second/every 15 minute) for three hours. The polymerization reaction was stopped by addition of amount of barium chloride equivalent to the amount of initiator. Barium bisulphite was precipitated and the reaction mixture was filtered to separate the inorganic precipitate. The filtrate was treated with acetone to get polyacrylamide precipitate in a pure state. The obtained polymer was then characterized by viscosity average molecular weight  $(\overline{M}_{\nu})$ determination, and elemental analysis. The percentage conversion after three hours of the polymerization reaction, element analysis, molecular weight (viscosity average molecular weight and degree of polymerization are summarized in Tab. I).

#### 2.2.2. Poly(propenoyl glycine)

In a well stoppered conical flask (250 ml capacity),  $10^{-4}$  mole (1 g) polyacrylamide (sample C) was dissolved in 100 ml absolute alcohol, then  $10^{-4}$  g mol (0.01 g) of  $\alpha$ -chloroacetic acid was added, then a few drops of piperydine were added as a catalyst. The reaction was continued for 4 hours at 40°C, then at room temperature for 24 hours. A white polymer precipitate was produced and filtered. The element analysis of the prepared polymer is summarized in Table II.

Infrared Spectroscopic Studies of Poly(propencyl glycine) [25] The infrared spectrum of the prepared polymer (sample D) is presented in Figure 1. The broad band at  $3424 \,\mathrm{cm}^{-1}$  could be attributed to the presence of OH group in (COOH). The weak band at  $2761 \text{ cm}^{-1}$  is due to symmetric vibration of aliphatic methylene group, while the two medium bands at 2676 and 2491  $\text{cm}^{-1}$  are attributed to the symmetric stretching vibrations of aliphatic methine group. The three weak absorption bands at 1870, 1842 and  $1826 \,\mathrm{cm}^{-1}$  could be attributed to the symmetric stretching vibrations for carbonyl group of the carboxylic acids. A series of bands in the region  $1668 - 1510 \text{ cm}^{-1}$  are attributed to the first and second group of bands for amide group (mainly C=O stretching vibrations and N-H deformation), while the two bands appearing at 1453 and  $1402 \,\mathrm{cm}^{-1}$  are attributed to the bending vibrations of methylene group. The two bands at 1094 and  $1042 \,\mathrm{cm}^{-1}$  could be attributed to the symmetric stretching vibration of carbonyl group.

<sup>1</sup>H-NMR Spectroscopic Studies of Poly(propenoyl glycine) [26] The <sup>1</sup>H-NMR signals of the prepared polymer (sample D) have been recorded in dimethyl sulphoxide with tetramethyl silane as internal reference. The proton NMR-spectrum is presented in Figure 2. The solvent protons appear as two singlet signals at  $\delta = 2.5$  ppm and  $\delta = 3.5$  ppm. The triplet signal at  $\delta = 1.6-1.8$  ppm is due to the methylene group

Some physical and analytical properties of polyacrylamide prepared by aqueous polymerization using different initiator concentration at	
TABLE I 40°C	

	Degree of	polymerization $(D_p)$	1280	562	369
	$\overline{M}_{\nu} \cdot 10^{-4}$	(lom/g)	3.461	1.523	1.000
	(%)	Found	20.000	20.500	19.300
	N(	Req.	19.718	19.718	19.718
Element analysis	C(%) $H(%)$	Found	6.600	6.900	7.200
		Req.	7.042	7.042	7.042
		Found	49.500	50.500	51.000
		Req.	50.704	50.704	50.704
	Percentage	conversion (%)	70	75	84
	NaHSO <sub>3</sub>	(g mol/L)	0.01	0.05	0.10
		No.	A	B	c

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			Elemen	t analysis				
	с С	(%)	)H(	(%)	N(	(%)	$\overline{M}_{v} \cdot 10^{-4}$	Degree of
Polymer name	Req.	Found	Req.	Found	Req.	Found	(g/mol)	polymerization $(D_p)$

369

5.867

19.200

18.805

3.950

4.403

37.302

37.773

Poly(propenoyl glycine)

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FIGURE 1 Infrared spectrum of poly(propenoyl glycine) sample.



FIGURE 2 <sup>1</sup>H-NMR spectrum of poly(propenoyl glycine) sample.

in the main polymeric chain, while the multiplet signal at  $\delta = 2.0-2.6$  ppm is due to the methine group proton overlapped with the solvent proton signal. The multiple signal at  $\delta = 3.5-4.9$  ppm could be attributed to the methylene group protons of the side chain group. The multiplet signal at  $\delta = 5.9-8$  ppm is due to (NH) group proton, while the singlet signal at  $\delta = 10.5$  ppm is due to the carboxylic group proton which disappeared after addition of deutrated water.

From the above investigations the suggested structure of the prepared polymers can be represented in the following scheme.



#### 3. RESULTS AND DISCUSSION

#### 3.1. Corrosion Behaviour of Tin in NaCl Solution

The effect of various concentrations (0.5 to 30 ppm) of polyacrylamide samples which have different molecular weight (polymer A = $3.4 \times 10^4$ , B =  $1.5 \times 10^4$  and C =  $1 \times 10^4$  g mol<sup>-1</sup>) and poly(propenoyl glycine) (polymer D) which has the same  $D_p$  of polymer C, on the corrosion behaviour of tin in 1 M NaCl solution was investigated at 20°C by using potentiodynamic polarization technique. The potentiodynamic polarization curves for tin in 1M NaCl solution in the absence and presence of the polymers A, B, C and D are given in Figures 3-6 respectively. These curves were swept from -1600 up to -300 mV (vs. SCE) with scan rate of  $100 \text{ mV s}^{-1}$ . Inspection of the data reveals that, in the absence of the polymer additives, the anodic sweep exhibits active passive transition. The active dissolution region displays two anodic peaks AI and AII prior to permanent passive region. The passive region is limited by pitting at a certain pitting potential  $(E_{pit})$  at which the passive current density suddenly rises sharply without any sign for oxygen evolution indicating breakdown of the passive film and initiation of visible pitting corrosion.

As mentioned before by Ammar *et al.* [27], tin dissolves anodically at first as Sn(II). The appearance of the first peak AI is related to the formation of  $Sn(OH)_2$  while the second anodic peak AII can be ascribed to the formation of  $Sn(OH)_4$  film. The formation of  $Sn(OH)_4$  may take place either by direct oxidation of the metal or by



FIGURE 3 Potentiodynamic polarization curves for tin in 1M NaCl containing different concentrations of polymer A at 20°C with scan rate of  $100 \text{ mV s}^{-1}$ .

conversion of  $Sn(OH)_2$  to  $Sn(OH)_4$ . The height of peak AI is greater than that of peak AII. It is possible that the formed  $Sn(OH)_4$  film dehydrated with increasing the anodic potential to a more thermodynamically stable  $SnO_2 \cdot xH_2O$  film of different degree of hydration [28]. The transformation of  $Sn(OH)_4$  to  $SnO_2 \cdot xH_2O$  is an irreversible process [29].

The initiation of pitting corrosion can be attributed to competitive adsorption between the aggressive  $C\overline{I}$  ions and the passivating  $O\overline{H}$ or  $O_2$  species at adsorption sites on the oxide covered surface. At  $E_{pit}$ , the Cl ions display the passivating species at some locations and promote local anodic dissolution, thereby causing a pit nucleus. Following this a pit growth occurs rapidly as a result of increasing the  $C\overline{I}$  ion concentration and hydrolysis of the pitting corrosion products inside the pits [30].



FIGURE 4 Potentiodynamic polarization curves for tin in 1M NaCl containing different concentrations of polymer B at  $20^{\circ}$ C with scan rate of  $100 \text{ mV s}^{-1}$ .

It is clear that the presence of various concentrations of the polymers in 1M NaCl solution has a great effect on both the cathodic and anodic polarization curves. The open circuit corrosion parameters (corrosion current,  $I_{corr}$  and corrosion potential  $E_{corr}$ ) as well as the anodic corrosion parameters (peak current of peak AI,  $I_{PAI}$  and pitting potential,  $E_{pit}$ ) in the absence and presence of the additives were determined from the polarization curves and given in Table III.

Regarding the obtained data, it is seen that the presence of polymer A which has the highest molecular weight decreases both the cathodic and anodic overpotentials and accelerates both the open circuit and anodic corrosion. The acceleration effect enhances with increased polymer concentration. However, polymers B, C and D act as corrosion



FIGURE 5 Potentiodynamic polarization curves for tin in 1M NaCl containing different concentrations of polymer C at  $20^{\circ}$ C with scan rate of  $100 \text{ mV s}^{-1}$ .

inhibitors. The inhibition efficiency (P%) of the three polymers on the open circuit corrosion was calculated by the following equation:

$$P\% = 100 \left( 1 - \frac{I_{\rm corr}}{I_{\rm corr}^0} \right) \tag{1}$$

where  $I_{corr}$  and  $I_{corr}^{o}$  are the corrosion current densities of the inhibited and uninhibited electrode respectively. The P% values are given in Table III. The plots of P% versus the logarithmic concentration of the inhibitors are illustrated in Figure 7. It is clear that the inhibition efficiency of these polymers increases with the increase in their concentration. Inhibition by these polymers can be explained by a



FIGURE 6 Potentiodynamic polarization curves for tin in 1M NaCl containing different concentrations of polymer D at  $20^{\circ}$ C with scan rate of  $100 \text{ mV s}^{-1}$ .

substitutional adsorption of the polymers according to the following equation [31].

$$Polymer_{aq} + xH_2O_{ads} \rightarrow polymer_{ads} + xH_2O_{aq}$$
(2)

These polymers inhibit mainly the cathodic reaction, acting therefore as cathodic inhibitors for the open circuit corrosion.

The data imply that polymer C has higher inhibition efficiency than polymer B, indicating that inhibition by the two polymers decreases with an increase of their molecular weight. Adsorption of these two polymer on the metal surface occurs via their  $\begin{pmatrix} -C & -NH_2 \\ \parallel \\ O \end{pmatrix}$  group while the hydrocarbon parts protrude brush-like in the solution.

Polymer type	Concentration ppm	$I_{corr}$ $\mu A \ cm^{-2}$	$E_{corr}$ V	I <sub>PAI</sub> mA cm <sup>-2</sup>	$E_{pit} \ V$
A	0.0 0.5 3.0 5.0 10.0 30.0	55.6 152.9 182.0 196.1 387.5 502.0	-1.07 -1.06 -1.08 -1.04 -1.05 -1.06	2.4 1.6 2.4 2.6 4.7 5.4	$-0.43 \\ -0.41 \\ -0.40 \\ -0.37 \\ -0.39 \\ -0.42$
В	0.0	55.6	-1.07	2.4	-0.43
	5.0	29.2	-1.30	1.2	-0.45
	10	26.4	-1.17	1.2	-0.45
	30	20.2	-1.08	1.3	-0.39
С	0.0	55.6	-1.07	2.4	-0.43
	5.0	27.6	-1.11	1.7	-0.42
	10	23.9	-1.13	1.6	-0.43
	30	22.0	-1.15	1.2	-0.45
D	0.0	55.6	-1.07	2.4	-0.43
	1.0	48.1	-1.11	1.8	-0.44
	5.0	16.9	-1.04	1.5	-0.42
	10	12.81	-1.05	1.0	-0.38
	30	1.80	-1.00	0.6	-0.36

TABLE III Electrochemical parameters for tin electrode in 1M NaCl containing various concentrations of polymer A, B, C and D at  $20^{\circ}$ C

However, polymer D shows the strongest inhibition even though it has the same  $D_p$  as polymer C. Such behaviour is likely related to the introduction of (-CH<sub>2</sub>-COOH) beside the presence of  $\langle -C - NH \rangle$ 

 $\begin{pmatrix} -\mathbf{U} - \mathbf{N}\mathbf{H} \\ \| \\ \mathbf{O} \end{pmatrix}$  in the polymer molecule.

For the studied inhibitors B, C and D, it was found that the experimental data fits Flory-Huggins adsorption isotherm which is given by the following equation [32]:

$$Log(\theta/C) = log xK + x log(1 - \theta)$$
(3)

where K is the equilibrium constant of adsorption process, x is the number of adsorbed water molecules replaced from the metal surface by adsorption of one polymer inhibitor and  $\theta$  is the surface coverage  $(\theta = P\%/100)$ .

Figure 8 represents the Flory-Huggins adsorption plot for the polymer inhibitors. The data gave straight lines with a slope of x and intercept of log xK. The constant value of K is related to the standard









free energy of adsorption  $\Delta G_{ads}^o$  by the following equation:

$$\mathbf{K} = 1/55.5 \exp\left(\frac{-\Delta G_{\mathrm{ads}}^o}{\mathbf{R}T}\right) \tag{4}$$

where 55.5 is the concentration of water in the solution in  $moll^{-1}$ . The calculated value of x, K and  $-\Delta G_{ads}^o$  are given in Table IV. It was found that the calculated standard free energy of adsorption vary from  $-8.4 \text{ kJ mol}^{-1}$  for polymer B to  $-7.1 \text{ kJ mol}^{-1}$  for polymer D, which is the strongest inhibitor of the investigated polymers. It is also clear from Table IV that the magnitude of K is the determining factor for the inhibition efficiency. The values of x are approximately five for polymers B and C indicating that each adsorbed molecule of the inhibitor replaces 5 adsorbed water molecules, while in case of polymer D, the value of x equal 0.5 indicating that two inhibitor molecules replace one adsorbed water molecule. Moreover, the presence of the polymers B, C or D inhibits also the anodic active dissolution of tin in 1M NaCl at 20°C as indicated by the decreases in the height of the peak current  $(I_{PAI})$  of the peak AI. Data in Table III show that the inhibition efficiency of these polymers towards the anodic active dissolution of tin is enhanced with the increases in the polymer concentrations. Also, the inhibition efficiency of the studied inhibitors against active dissolution of tin decreases in the order: D > C > B. On the other hand, the presence of these polymers have no significant effect on pitting corrosion of tin in 1M NaCl solution at 20°C.

#### 3.2. Effect of Temperature on Inhibition Characteristics of the Polymer D

The effect of temperature  $(20-50^{\circ}C)$  on the potentiodynamic polarization curves of tin in 1M NaCl in the absence and presence of 10 ppm of the polymer D was investigated and the results are shown

polymer absorption on tin from TM NaCl at 20°C					
Polymer			$\Delta G^o_{ads}$		
type	x	K	$KJ mol^{-1}$		
В	5.5	0.57	-8.4		
C	4.5	0.57	-8.41		
D	0.5	0.33	-7.1		

TABLE IV Thermodynamic parameters (according to Flory-Huggins isotherm) for the polymer absorption on tin from 1M NaCl at  $20^{\circ}C$ 

in Figures 9 and 10 respectively. The electrochemical parameters are given in Table V. It is seen that  $I_{corr}$  increases,  $E_{corr}$  shifts to more negative direction and  $I_{PAI}$  increases with raising the temperature in the absence and presence of the polymer inhibitor. Increasing the temperature has no significant effect on  $E_{pit}$ . The inhibition efficiency P% of the inhibitor D under open circuit condition was calculated at different temperatures and the data are given in Table V. It is obvious that the open circuit and active anodic dissolution of tin in 1M NaCl increase and consequently the inhibition efficiencies with increased temperature. The change in the inhibition efficiencies with temperature may be ascribed to desorption of some adsorbed inhibitor molecules from the surface. This suggests that physical adsorption may be the type of adsorption of the inhibitor on the metal surface. The apparent activation energy  $(E_a)$  for the open circuit corrosion reaction of tin in 1M NaCl in the absence and



FIGURE 9 Potentiodynamic polarization curves for tin in 1M NaCl at different temperature with scan rate of  $100 \text{ mV s}^{-1}$ .



FIGURE10 Potentiodynamic polarization curves for tin in 1M NaCl containing 10 ppm of polymer D at different temperatures with scan rate of  $100 \text{ mV s}^{-1}$ .

TABLE V Electrochemical parameters for tin electrode in 1M NaCl in the absence and presence of 10 ppm of polymer D at different temperatures

Polymer type and concentration	Temperature (°C)	$I_{corr}$ (A cm <sup>-2</sup> )	$E_{corr}$ (V)	$I_{PAI}$ (mA cm <sup>-2</sup> )	$E_{pit}$ (V)
	20	55.6	-1.07	2.4	-0.43
_	30	83.8	-1.09	1.9	-0.38
	40	127.5	-1.11	3.1	-0.38
	50	195.7	-1.23	5.1	-0.39
	20	12.8	-1.05	1.0	-0.38
Polymer D	30	29.2	-1.07	2.5	-0.38
(10 ppm)	40	87.7	-1.07	2.7	-0.37
× 11	50	124	-1.08	2.8	-0.37

presence of 10 ppm of the polymer D were calculated from Arrhenius equation:

$$I_{\rm corr} = A e^{-E_a/RT} \tag{5}$$

where R is the universal gas constant and A is Arrhenius preexponential factor. A plot of  $\log I_{corr}$  vs. 1/T gave straight lines as shown in Figure 11. The values of  $E_a$  obtained from the slope values of lines are given in Table VI. It is obvious that the effective activation energy of the inhibited solution is higher than that in the free NaCl



FIGURE 11 Arrhenius plots of the corrosion rate for tin in 1M NaCl solutions in the absence and presence of polymer D.

TABLE VI Activation parameters for open circuit corrosion of tin in 1M NaCl in the absence and presence of 10 ppm of polymer D

	1M NaCl		1MNaCl + 10 ppm of polymer D			
$\frac{E_a}{KJ  mol^{-1}}$	$\frac{\Delta H^o}{KJ  mol^{-1}}$	$\Delta S^o \ JKmol^{-1}$	$E_a$ KJ mol <sup>-1</sup>	$\Delta H^o \ KJ  mol^{-1}$	$\Delta S^o$ JK mol <sup>-1</sup>	
14.56	13.3	-106	26.8	25.6	-22.8	



FIGURE 12 Transition state equation plots of the corrosion rate for tin in 1M NaCl solutions in the absence and presence of polymer D.

solution. An alternative formulation of the Arrhenius equation is the transition state equation:

$$I_{\rm corr} = {\rm R}T/{\rm Nh} \exp\left(\frac{\Delta S^o}{{\rm R}}\right) \exp\left(\frac{-\Delta H^o}{{\rm R}T}\right) \tag{6}$$

where h is plank's constant, N is Avogadro's number,  $\Delta S^o$  is the entropy of activation and  $\Delta H^o$  is the enthalpy of activation. A plot of log  $I_{\rm corr}/T$  vs. 1/T gave a straight line (Fig. 12) with a slope of  $-\Delta H^o/2.303$  R and an intercept of (log R/NH +  $\Delta S^o/2.303$  R) from which the values of  $\Delta S^o$  and  $\Delta H^o$  were calculated and the values are listed in Table VI. The value of  $\Delta H^o$  reflects the exothermic nature of the corrosion process under open circuit condition.

#### 4. CONCLUSIONS

In conclusion, the above data revealed the following:

- (1) In the absence of polymer additives, the cathodic current density decreases continually with the applied potential and the anodic sweep exhibits active passive transition.
- (2) The presence of polymer A which has the highest molecular weight of the polyacrylamide series decreases both the cathodic and anodic overpotentials and accelerates both the open circuit and anodic corrosion.
- (3) The presence of polymers B, C and D acts as corrosion inhibitors and the inhibition efficiency increases with decreasing molecular weight, and polymer D gives the highest inhibition efficiency (96.8%) when 30 ppm of it is used in 1M NaCl solution at 20°C.
- (4) These types of water soluble polymeric materials have been shown to be low cost, easily prepared and stable corrosion inhibitors.

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