Inhibition Effect of Some Polymers on the Corrosion of Cadmium in a Hydrochloric Acid Solution

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ABSTRACT: The effects of poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), sodium polyacrylate (NaPA), poly(ethylene glycol) (PEG), pectin (P), and carboxymethyl cellulose (CMC) on the corrosion of cadmium in a $0.5M$ hydrochloric acid (HCl) solution were studied with both electrochemical impedance spectroscopy and Tafel plot techniques. Measurements were carried out at cathodic, open-circuit, and anodic potentials. All the investigated polymers had inhibitory effects on both the cathodic (except for NaPA, P, and CMC) and anodic processes, with a predominant anodic inhibiting action. However, NaPA, P, and CMC exhibited a slight cathodic inhibiting action only at higher polymer concentrations. This behavior may be attributed to the very weak adsorbability of the polymers on the cathodic sites. Because PVA and PEG had hydroxy groups, there could be bridging between the polymer and the surface, resulting in an inhibiting effect in the HCl solution. However, PVA had much greater adsorbability on the surface than PEG at the anodic potential. The adsorption of most of the polymers obeyed a Temkin adsorption isotherm, and this indicated indicating that the main process of inhibition was adsorption. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 866–871, 2003

Key words: adsorption; films; water-soluble polymers

INTRODUCTION

Cadmium and its alloys have found extensive applications in industry (e.g., as coatings for steel and aluminum that provide surface protection). Despite numerous publications on cadmium in alkaline solutions containing organic compounds,[1] very little work has been done on the corrosion inhibition of cadmium in acidic media.[2–4] Very small amounts of certain water-soluble polymers are known to be effective in inhibiting the corrosion of ferrous materials in contact with water. These polymers, in amounts ranging from 5 × 10⁻⁶ to 2 wt %, remove the products of corrosion formed before treatment and effectively prevent further corrosion.[5]

It is interesting to analyze the adsorption of macromolecules at the metal surface and the adsorption of small organic molecules. The study of the behavior of macromolecular chains in solution and, in particular, at the metal–solution interface seems to be very important.[6–8] The presence of polymers in various media mostly inhibits the processes in the active region of iron passivation.[9,10] Poly(acrylic acid) (PAA) is adsorbed mainly on the active surfaces of bare metal.[11,12] The behavior of the corrosion inhibition of steels, by various cationic and anionic polymers, was investigated by Sekine et al.[13] The results showed that cationic polymers lack inhibition ability, whereas anionic polymers have a more effective inhibition ability. Previous work[14] on this subject was focused on the problems of the conformational behavior of PAA and its derivatives adsorbed on iron in H_2SO_4 solutions.

This study tested the influence of various polymers, including pectin (P), carboxymethyl cellulose (CMC), poly(vinyl alcohol) (PVA), poly(ethylene glycol) (PEG), PAA, and sodium polyacrylate (NaPA), on the corrosion of cadmium in hydrochloric acid (HCl) solutions with Tafel plot extrapolation and electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL

A solution of HCl ($0.5M$) was prepared from an Analar reagent and twice distilled water and was deaerated with oxygen-free nitrogen for at least 5 h. Measurements were performed on a planar cadmium disc electrode (area = 0.125 cm²; 99.999% specpure grade; Aldrich) embedded in an Araldite holder. Before each measurement, the electrode was polished with successive grades of emery papers, degreased in pure ethanol, and washed in running and twice distilled water before being inserted into the polarization cell. The reference electrode was a saturated calomel electrode to which all potentials were referred. The cell description has been given elsewhere.[15]
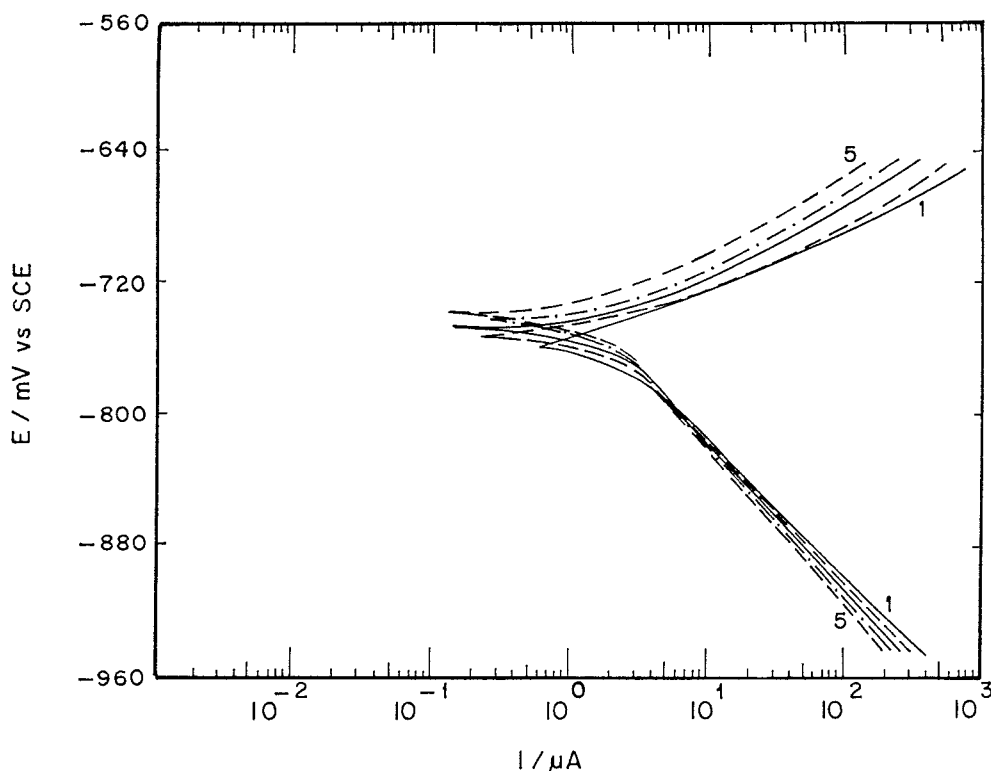
Figure 1 Tafel plots for cadmium in 0.5M HCl (dE/dt = 1 mV s^{-1}) and in the presence of PVA [(1) 0.0, (2) 2 × 10^{-2}, (3) 4 × 10^{-2}, (4) 1 × 10^{-1}, and (5) 2 × 10^{-1} g dm^{-3}].

The EIS measurements were carried out in a frequency range of 10 kHz to 0.2 Hz. An amplitude of 5 mV peak to peak was used for the alternating-current signal for all EIS measurements. The Tafel plot technique was carried out in a potential range of −200 to +50 mV with respect to the open-circuit (OC) potential. Simultaneous EIS and Tafel plot measurements were carried out on the cadmium electrode in 0.5M HCl solutions with and without the additive polymers at 30°C with a potentiostat/galvanostat (model 273A), a frequency response analyzer (model 5208), and a personal computer. Details of the experimental procedures have been described elsewhere.[16]

Reagent-grade P (Aldrich), CMC, PVA, PEG, PAA, and NaPA were used without further purification. The polymer solution was prepared by the dissolution of the appropriate amount (0.05 g) in 10 mL of twice distilled water. The desired volume was added to the electrolyte (250 mL).

RESULTS AND DISCUSSION

Figure 1 represents polarization curves for cadmium in 0.5M HCl with and without the addition of different PVA concentrations. The presence of PVA results in a marked shift in the anodic branches and a slight shift in the cathodic branches of the polarization curves toward lower current densities. The positive shift in the corrosion potential (E_{corr}) indicates that the anodic process is much more affected than the cathodic process. This suggests that PVA acts predominantly as an anodic inhibitor. The fact that the Tafel slopes of the anodic and cathodic processes (b_c and b_a, respectively) in Table I are almost the same in uninhibited and

TABLE I
Tafel Parameters (b_c and b_a) and i_{corr} Values Obtained by Tafel Extrapolation and Polarization Resistance Methods on Cadmium in 0.5M HCl Without and with the Addition of PVA at E_{corr} (30°C)

Additive concentration (g dm^{-3})	Tafel extrapolation method			Impedance method
	b_c/mV (decade)$^{-1}$	b_a/mV (decade)$^{-1}$	i_{corr}/μA (cm^{-2})	i_{corr}/μA (cm^{-2})
0	100	48	24	26
2 × 10^{-2}	103	49	21	24
4 × 10^{-2}	105	50	19	22
1 × 10^{-1}	105	50	18	20
2 × 10^{-1}	106	50	17	19

TABLE II
Effect of Some Polymers on the Impedance Parameters of the Cadmium Electrode
in 0.5*M* HCl Solution at Cathodic, OC, and Anodic Potentials

Polymer	Additive concentration (g dm^{-3})	E_{corr} (mV)	At −200 mV				At 0.0 mV				At 50 mV			
			R_S (Ω)	R_P (Ω)	C_{dl} (μF)	I (%)	R_S (Ω)	R_P (Ω)	C_{dl} (μF)	I (%)	R_S (Ω)	R_P (Ω)	C_{dl} (μF)	I (%)
	0	−750	15	590	20	—	3	4300	22	—	2	230	70	—
	2×10^{-2}	−747	15	670	19	11.9	3	4800	20	10.41	2	442	45	48.5
PVA	4×10^{-2}	−743	15	750	17	21.3	3	5200	18	17.3	2	1009	33	77.2
	1×10^{-1}	−740	15	830	15	28.9	3	5900	16	27.1	2	1312	25	82.5
	2×10^{-1}	−738	15	910	13	35.1	3	6200	11	30.6	2	1460	20	84.2
	0	−750	15	590	20	—	3	4300	22	—	2	230	70	—
	2×10^{-2}	−751	15	710	18	16.9	3	4600	21	6.5	2	320	47	28.1
PAA	4×10^{-2}	−755	15	790	16	25.3	3	5000	19	14	2	620	36	64.6
	1×10^{-1}	−753	15	880	14	33	3	5600	17	23.2	2	930	28	75.2
	2×10^{-1}	−755	15	1020	14	42.2	3	5950	15	29.4	2	1100	25	79.1
	0	−750	16	590	20	—	3	4300	22	—	2	230	70	—
	2×10^{-2}	−750	16	590	20	—	3	4500	21	4.4	2	292	49	21.2
NaPA	4×10^{-2}	−748	16	590	20	—	3	4900	19	12.2	2	550	38	58.2
	1×10^{-1}	−747	16	620	19	4.8	3	5520	18	22.1	2	819	30	71.6
	2×10^{-1}	−746	16	650	18	9.2	3	5830	16	26.2	2	905	28	74.6
	0	−750	15	590	20	—	3	4300	22	—	2	230	70	—
	2×10^{-2}	−752	15	790	18	25.3	3	4670	21	7.9	2	270	50	14.2
PEG	4×10^{-2}	−753	15	830	16	28.9	3	5100	19	15.7	2	492	41	53.2
	1×10^{-1}	−734	15	920	14	35.9	3	5750	18	25.2	2	710	33	67.6
	2×10^{-1}	−755	15	1070	12	44.9	3	6050	16	28.9	2	805	30	71.4
	0	−750	15	590	20	—	3	4300	22	—	2	230	70	—
	2×10^{-2}	−750	15	590	20	—	3	4470	22	3.8	2	260	53	11.5
P	4×10^{-2}	−749	15	590	20	—	3	4870	20	11.7	2	390	45	41
	1×10^{-1}	−748	15	600	19	1.7	3	5380	19	20	2	610	36	62.3
	2×10^{-1}	−748	15	620	18	4.8	3	6750	17	36.3	2	708	35	67.5
	0	−750	15	590	20	—	3	4300	23	—	2	230	70	—
	2×10^{-2}	−750	15	590	20	—	3	4420	22	2.7	2	238	57	3.4
CMC	4×10^{-2}	−749	15	590	20	—	3	4600	20	6.8	2	294	52	21.8
	1×10^{-1}	−750	15	590	20	3.2	3	4720	19	8.9	2	505	41	54.5
	2×10^{-1}	−748	15	650	18	9.2	3	4820	18	10.8	2	608	39	62.5

inhibited solutions suggests that the inhibitory action of PVA reduces the surface area available for hydrogen evolution and anodic cadmium dissolution without affecting their mechanism.

The EIS data obtained for cadmium in 0.5*M* HCl in the absence and presence of the different additive polymers (P, CMC, PVA, PEG, PAA, and NaPA) in the concentration range of 2×10^{-2} to 2×10^{-1} g dm^{-3} are given in Table II. The results demonstrate that the added polymers have a negligible influence on the R_S values. Furthermore, the observed polarization resistance in the presence of the additives (R_P) increases, whereas the double-layer electrode capacitance (C_{dl}) is noticeably diminished. The inhibition efficiency (I) of the investigated polymers can be calculated from the following relation:

$$I\% = 100 (R_P - R_P^o)/R_P$$

where R_P^o represent the polarization resistance in the absence of the additives. The I value of the additives at the cathodic potential is small in comparison with the values at the anodic potential. This view is reinforced

by a comparison of the values of both R_P and C_{dl}, as depicted in Table II. A careful examination of these results suggests that the investigated additives are predominantly anodic inhibitors. Figure 2 presents a complex-plane impedance diagram for a cadmium electrode in 0.5*M* HCl in the presence of various concentrations of PVA in the anodic potential region at 30°C. The equivalent circuit model in Figure 3(a) is given as a simplified equivalent circuit model in Figure 3(b). The measured complex-plane impedance plot is similar to that calculated by the equivalent circuit model. The corrosion current density (i_{corr}) data have been calculated with the R_P value obtained from impedance measurements, along with the Stern–Geary equation:

$$i_{corr} = \frac{b_a b_c}{2.303 R_P A (b_a + b_c)}$$

where R_P is equal to $\lim_{F \to 0}(Z^- - R_S)$ and A is the electrode surface area. The observed i_{corr} values (Table I) obtained from Tafel extrapolation are in good agree-
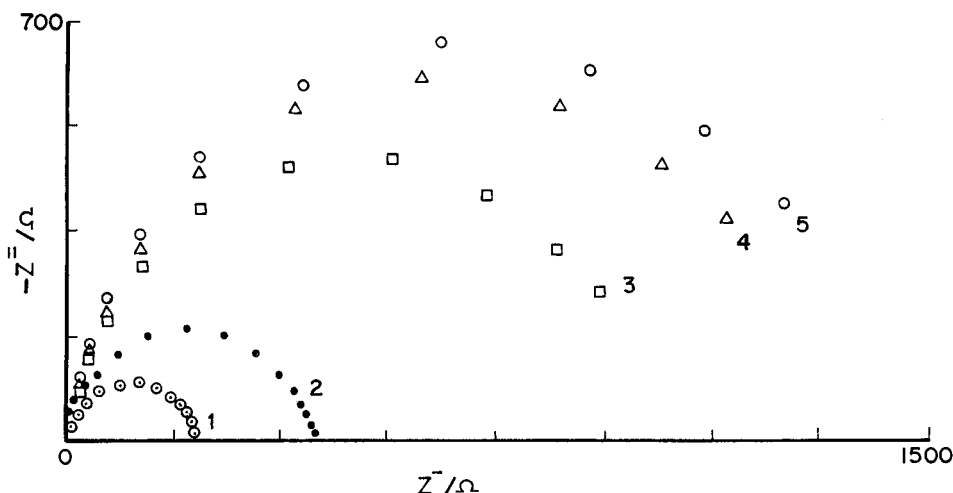
Figure 2 Complex-plane impedance of cadmium in a 0.5*M* HCl solution at the anodic potential (+50 mV vs OC) in the presence of PVA [(1) 0.0, (2) 2×10^{-2}, (3) 4×10^{-2}, (4) 1×10^{-1}, and (5) 2×10^{-1} g dm^{-3}].

ment with those calculated from the polarization resistance of the impedance measurements at E_{corr}. The foregoing results confirm the recent discussion concerning the use of impedance measurements as a fast and sensitive technique of testing inhibitor efficiency.[17] A comparison of the investigated additive polymers at the highest examined concentrations revealed the order of decreasing inhibitory effect, particularly in the anodic potential region:

$$PVA > PAA > NaPA > PEG > P > CMC$$

The decreased values of C_{dl} with increasing additive concentrations can be explained by the fact that the surface of the electrode is covered with some solid film, the inhibiting species, or both.[18] On the basis of these results, we can conclude that the anodic dissolution process is more strongly affected by the addition of polymers than the cathodic process. These results suggest that retardation of the electrode processes occurs, especially at anodic sites, as a result of the coverage of the majority of active sites of the cadmium surface by the polymer molecules. There-

fore, inhibition via the formation of metal–polymer complexes can be expected.[14] Furthermore, the fact that the dissolution of metals is generally inhibited by the polymer additives explains the formation of scarcely soluble complexes[19] on the metal surface. However, the variation of I (%) of the investigated polymers can be attributed to the structures and types of the polymers.[13] Therefore, some examined polymers such as CMC, P, PAA, and NaPA with carboxylic groups (—COOH) can be adsorbed, forming a film that inhibits the corrosion of cadmium. However, PVA and PEG have hydroxy groups, and there may be bridging between the polymer and the surface of the electrode,[20] resulting in an inhibiting effect in HCl solutions. Moreover, PVA has much greater adsorbability on the electrode surface than PEG at the anodic potential. This behavior could be ascribed to the closely packed film formation on the surface[21] by PVA. Therefore, we can suggest that a very strong and poorly conducting film is formed on the metal surface in the presence of the PVA additive. The observed small shift in E_{corr} in the presence of some of the
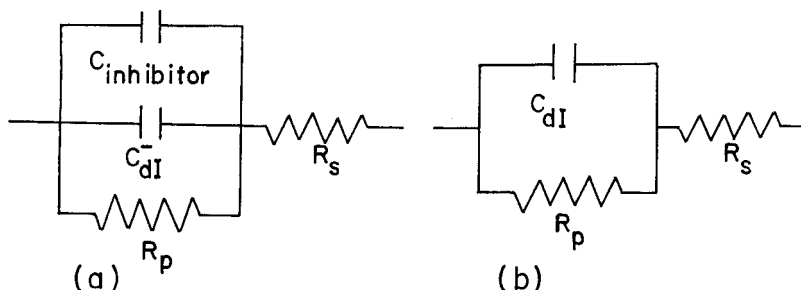
Figure 3 (a) Equivalent model and (b) simplified equivalent circuit model. $C_{inhibitor}$ is the capacitance of the parts in which the inhibitors are adsorbed, C_{dl}^{-} is the capacitance of the parts in which the inhibitors are not adsorbed, and C_{dl} is the apparent double-layer capacitance.
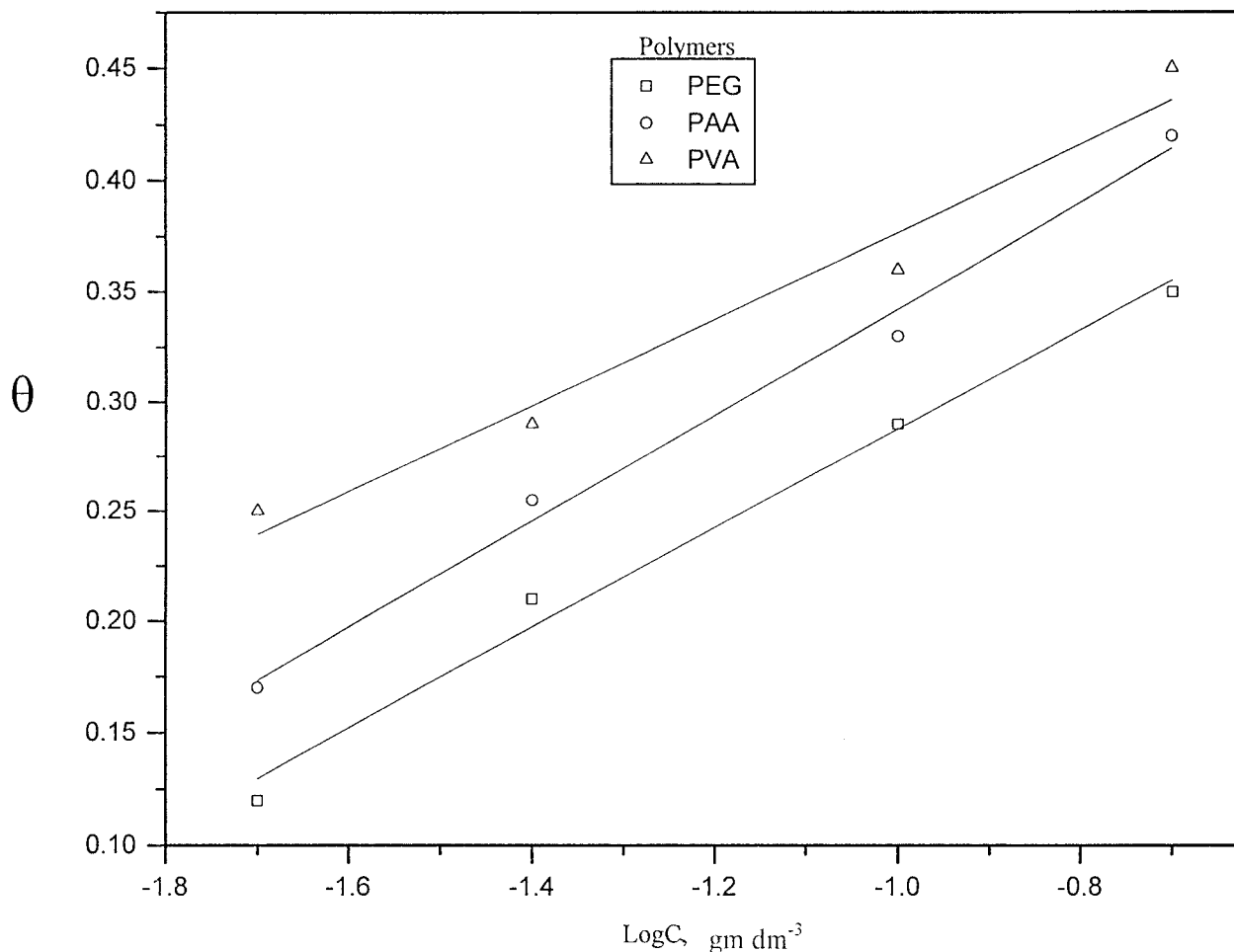
Figure 4 Temkin adsorption isotherm for some polymers on cadmium in $0.5M$ HCl solution in cathodic potential region at 30°C.

examined polymers does not reflect any special inter-action, although these inhibitors decrease C_{dl} values and increase R_P values. This suggests that the inhibit-ing action of these compounds occurs by simple block-ing at the cadmium surface.[22] It is well known that Cl^- ions enhance the adsorption of polymer molecules at the surface of an electrode. These results also suggest that the inhibitory effect of the investigated polymers may be attributed to competitive adsorption of the inhibitory agent and aggressive ions at the adsorption sites on the metal surface.[23,24] A predominance of inhibitor adsorption occurs and, in turn, leads to pro-tection of the metal. However, this adsorption takes place through the functional groups[25,26] of the poly-mer. The results obtained, therefore, indicate a rather complex argument for the inhibitory effect of the poly-mers in HCl solutions. Similar results were obtained by El-Sayed[27] for the inhibitory effect of the investi-gated polymers for the corrosion of iron in various acidic solutions. Such compounds act as primary in-hibitors, with the presence of Cl^- ions increasing their efficiency. As mentioned previously,[11,12] the enhanced

efficiency of the investigated polymers in HCl and $HClO_4$ solutions may be due to the presence of a greater active surface area, which would, in turn, re-sult in a greater adsorbability of such polymers at the metal surface.

The extent of corrosion inhibition depends on the surface conditions and mode of adsorption of the in-hibitors.[28] Under the assumptions that the corrosion of the covered parts of the surface is equal to zero and that the corrosion takes place only on the uncovered parts of the surface, the degree of coverage (θ) has been calculated from $\theta = 1 - R_P^o/R_P$. The plot of θ against log C (g dm^{-3}; where C is the polymer con-centration) is linear in nature, as shown in Figure 4, and this suggests that the adsorption of PVA, PAA, and PEG on the cadmium surface obeys a Temkin isotherm.

CONCLUSIONS

1. I (%) increases as the polymer concentration is increased. The variations of I for the investi-

gated polymers under the same conditions can be attributed to the structures and types of the polymers.

2. Some of the investigated polymers (PVA, PAA, and NaPA) are strongly adsorbed on cadmium in HCl solutions, predominantly in the anodic region.

3. PVA has much greater adsorbability on the electrode surface than PEG, although the two investigated polymers have hydroxy groups. This behavior can be ascribed to the closely packed film formation on the surface, and a very strong and poorly conducting film is formed on the metal surface by PVA at the anodic potential.

4. The adsorption of most of the polymers obeys a Temkin adsorption isotherm, and this indicates that the main process of inhibition is adsorption.

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