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Synergistic influence of poly(4-vinylpyridine) and potassium iodide on inhibition of corrosion of mild steel in 1M HCl

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Abstract

The corrosion and inhibition behavior of mild steel in 1 M HCl in the presence of poly(4-vinylpyridine) (P4VP) and potassium iodide (KI) was investigated using weight loss measurements, potentiodynamic polarization studies and impedance measurements. The inhibition efficiency increased with increasing P4VP concentration. The inhibiting action of P4VP is considerably enhanced by the addition of potassium iodide. The adsorption of this compound either alone or in combination with iodide ions on the metal surface is found to obey Lamgmir's adsorption isotherm. The experimental results suggest that the presence of iodide ions in the solution increases the surface coverage θ and, therefore, indicate the joint adsorption of P4VP and iodide ions. On the other hand, it was found that the inhibiting effect of P4VP and (P4VP + KI) increased with increasing temperature of the corrosion medium. The presence of these species in the solution decreases the double layer capacitance and increases the charge transfer resistance, both derived from Nyquist plots obtained from a.c. impedance studies. The variation of charge transfer resistance with time suggests that the inhibitive action of (P4VP + KI) depends mainly on the protective inhibitor film formed on the steel surface.

1. Introduction

Acid solutions are widely used in industry the most important areas of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing [1]. Inhibitors are usually used in these processes to control the corrosion of the metal. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen [2–12]. For polymer inhibitors, the use of polyvinylpyridine, polyvinylbipyridine, polyvinylpyrolidone, polyethyleneimine and polyvinylimidazoles has been widely examined [13–20].

Poly(4-vinylpyridine) (P4VP) has been used as inhibitor of mild steel and iron in HCl [19, 21–23], of copper in 3 M HNO_3 [24], of zinc in 1 M H_2SO_4 [25], of iron in 1 M H_2SO_4 [26, 27] and of Cu60–Zn40 in 0.5 M HNO_3 [28]. In the present investigation, the synergistic influence of iodide ions on the performance of P4VP as a corrosion inhibitor of mild steel in 1 M HCl has been systematically studied by weight loss measurements, potentiodynamic polarization studies and impedance measurements.

2. Experimental

P4VP was prepared by radical polymerization of 4-vinylpyridine in methanol, under vacuum, with azobisisobutynitrile as initiating agent, as described previously [29]. The polymer was fractionated by partial precipitation from methanol–ethylacetate mixture solution. The structure was checked by ^{1}H-NMR and FTIR spectroscopy. The molecular weight was estimated by the viscosity technique using methanol as solvent [30]. Solution of 1 M HCl was prepared from an analytical reagent grade 37% HCl and bidistilled water and was used as corrosion media. For the weight loss measurements, the experiments were carried out in solutions of 1 M hydrochloric acid (uninhibited and inhibited) on mild steel containing 0.14% C, 0.21% Si, 0.01% Al, 0.012% S, 0.09% Mn, 0.006% Cu. Specimens in the form of discs with a diameter of 30 mm and a thickness of 2 mm were used. They were polished successively with different grades of emery paper up 1200 grade.

Each run was carried out in a glass vessel containing 50 ml test solution. A clean weighed mild steel sample was completely immersed at an inclined position in the vessel. After 1 h of immersion in 1 M HCl, with and without addition of inhibitor at different concentrations, the specimen was withdrawn, rinsed with bidistilled water, washed with acetone, dried and weighed. The weight loss was used to calculate the corrosion rate. Electrochemical experiments were carried out in a glass cell (CEC/TH-Radiometer) with a capacity of 500 ml. A platinum electrode and a saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode. The working electrode (WE) was in the form of a disc and was embedded in a Teflon rod with an exposed area of 0.95 cm^2.

Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were conducted in an electrochemical measurement system (VoltaLab40) which comprised a PGZ301 potentiostat, a personal computer and VoltaMaster4 software. The a.c. impedance measurements were performed at corrosion potentials (E_{corr}) over a frequency range of 10 kHz to 20 mHz, with a signal amplitude perturbation of 10 mV. Nyquist plots were obtained from the results of these experiments. Values of the charge transfer resistance R_t were obtained from the plots by determining the difference in the values of impedance at low and high frequencies as suggested by Tsura et al. [31]. Values of the double-layer capacitance C_{dl} were calculated from the frequency at which the impedance imaginary component -Z″ was maximum using the equation:

$$f(Zi_{max}) = \frac{1}{2\pi C_{dl} R_t} \tag{1}$$

Corrosion potentials and corrosion current densities were determined by extrapolating the cathodic and anodic Tafel regions from the potentiodynamic polarization curves, the intersect is the corrosion current and corrosion potential.

Inhibition efficiencies $P\%$ were calculated as follows:
– Weight loss measurement:

$$P\% = \frac{W - W'}{W} \times 100 \tag{2}$$

where W and W' are the corrosion rate of steel due to the dissolution in 1 M HCl in the absence and the presence of definite concentrations of inhibitor, respectively.
– Polarization measurements:

$$P\% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \tag{3}$$

where I_{corr} and I'_{corr} are the corrosion current densities in the absence and the presence of the inhibitor.
– Impedance measurements:

$$P\% = \frac{R_t^{-1} - R_t'^{-1}}{R_t^{-1}} \times 100 \tag{4}$$

where R_t and R'_t are the charge transfer resistance values without and with inhibitor, respectively.

3. Results and discussion

3.1. *Weight loss measurements*

Table 1 gives the values of inhibition efficiency obtained from the weight loss measurements for different concentrations of P4VP in 1 M HCl at 25 °C after 1 h immersion. The inhibition efficiency increases with increasing inhibitor concentration. The optimum concentration required to achieve an efficiency of 90% is found to be 100 mg l^{-1}. The inhibition by P4VP can be explained in terms of adsorption on the metal surface. The compound can be adsorbed by the interaction between the lone pair of electrons of the nitrogen atom of the pyridyl moiety and the metal surface. This process is facilitated by the presence of d π vacant orbitals of low energy in the iron atom, as observed in transition group metals. Moreover, the formation of positively charged protonated P4VP species in acidic solutions facilitates adsorption of the compound on the metal surface through electrostatic interactions between the organic molecules and the metal surface.

Table 2 gives the values of inhibition efficiency for the corrosion of mild steel in 1 M HCl in the presence of 5 mg l^{-1} P4VP and different concentrations of KI. The maximum synergistic effect is obtained for a KI concentration of 0.1%.

Table 3 gives the values of inhibition efficiency for different concentrations of P4VP in the absence and presence of 0.1% KI. The addition of KI improves the inhibition efficiency of P4VP significantly. The synergis-

Table 1. Inhibition efficiencies for corrosion of mild steel in 1 M HCl with different concentrations P4VP obtained from weight loss measurements at 25 °C

Concentration of P4VP /mg l^{-1}	Inhibition efficiency (P) /%
1	74.10
5	81.40
15	83.20
30	85.10
100	90.50

Table 2. Inhibition efficiency for different concentrations of KI of mild steel in 1M HCl in the presence of 5 mgl^{-1} of P4VP by weight loss measurements at 25 °C

KI concentration /%	Inhibition efficiency (P) /%
0.00	81.40
0.025	89.00
0.05	90.10
0.10	92.10
0.20	88.80
0.25	88.10

Table 3. Inhibition efficiencies for corrosion of mild steel in 1 M HCl with different concentrations of P4VP in presence of 0.1% KI at 25 °C, from by weight loss measurements

Concentration of P4VP /mg l^{-1}	Inhibition efficiency (P) /%
1	91.20
5	92.30
15	93.30
30	93.80
100	95.60

tic effect between P4VP and KI is due to interactions between chemisorbed I^- and organic polycations $P4VP^+$. The stabilization of adsorbed $P4VP^+$ on the surface, which may be exhibited by electrostatic interactions with I^- ions, leads to higher surface coverage and greater corrosion inhibition.

3.2. *Polarization measurements*

Figure 1 shows the polarization curves of mild steel in 1 M HCl blank solution and in the presence of different concentrations (1–100 mg l^{-1}) of P4VP. The increase in P4VP concentrations led to both anodic and cathodic current inhibition, but the reduction in the anodic current was more significant than that of the cathodic current. This shows that the addition of P4VP reduces anodic dissolution and also retards the hydrogen evolution reaction.

Table 4 gives the values of kinetic corrosion parameters as to the corrosion potential E_{corr}, corrosion current density I_{corr}, Tafel slopes b_a and b_c, and inhibition efficiency for the corrosion of mild steel in 1 M HCl with different concentrations of P4VP in the presence and absence of 0.1% KI. It can be concluded that:

- The E_{corr} values are shifted positively. In the presence of 0.1% KI, the values remain almost unchanged.
- The I_{corr} values decrease in the presence of different concentrations of P4VP. The addition of KI further reduces the I_{corr} values.

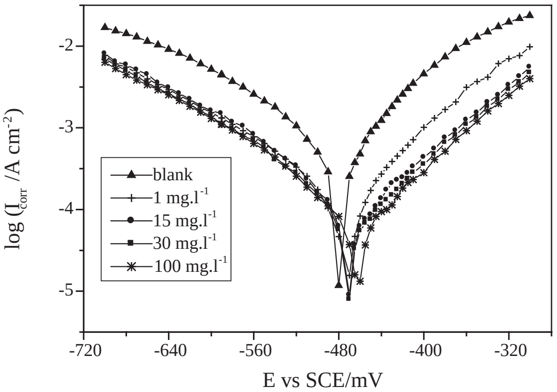

Fig. 1. Potentiodynamic polarization curves for mild steel in 1 M HCl containing different concentrations of P4VP.

Table 4. Potentiodynamic polarization parameters for corrosion of mild steel in 1 M HCl with various concentrations of P4VP in presence and absence of 0.1% KI at 25 °C

P4VP conc. /mg l^{-1}	KI conc. /%	E_{corr} vs$_{SCE}$ /mV	I_{corr} /μA cm^{-2}	b_a /mV dec^{-1}	b_c /mV dec^{-1}	P /%
Blank	–	−482	613	92	131	—
1	–	−472	110	73	110	82.00
1	0.1	−470	038	76	118	93.80
5	–	−474	100	80	110	83.68
5	0.1	−473	032	73	125	94.78
15	–	−470	070	76	115	88.58
15	0.1	−471	029	82	130	95.27
30	–	−465	065	80	120	89.10
30	0.1	−468	024	80	128	96.08
100	–	−461	048	76	110	92.07
100	0.1	−458	016	70	130	97.39

- Tafel lines of nearly equal slopes were obtained. This indicates [32] that the adsorbed molecules of P4VP do not affect the mechanism of either iron dissolution or hydrogen evolution. The addition of KI produces slight changes in the values of b_a and b_c.

The values of inhibition efficiency increase with increase in P4VP concentration reaching a maximum value at 100 mg l^{-1}. The addition of KI improved the inhibition efficiency of P4VP significantly.

The interaction of inhibitor molecules can be describe by introduction of an S synergism parameter [33], which is defined as

$$S = \frac{1 - E_{1,2}^{\mathrm{calc}}}{1 - E_{1,2}^{\mathrm{meas}}} \tag{5}$$

where $E_{1,2}^{\mathrm{calc}}$ is the calculated inhibition effect supposing additivity (no interaction between the inhibitor compounds exits). $E_{1,2}^{\mathrm{calc}}$ can be expressed by

$$E_{1,2}^{\mathrm{calc}} = E_1 + E_2 - E_1 E_2 \tag{6}$$

where $E_1 = 1 - I_1/I_0$, $E_2 = 1 - I_2/I_0$ and $E_{1,2}^{\mathrm{meas}} = 1 - I_{1,2}/I_0$, and I_1 is the corrosion current density for the anion (I^-) ; $I_{1,2}$ the measured corrosion current density for the P4VP + I^--containing solution; I_0 the corrosion current density for the blank solution. (The relationship between the commonly used P% inhibition efficiency and E is the following: $P\% = \mathrm{E} \times 100\%$.)

The expression for S can be simplified to

$$S = \frac{I_1 I_2}{I_{1,2} I_o} \tag{7}$$

S approaches 1 when no interaction between the inhibitor compounds exists, while $S > 1$ points to a synergistic effect. In the case of $S < 1$, the antagonistic interaction prevails, which may be attributed to competitive adsorption.

Values of S are given in Table 5. Most values are greater than unity. This result suggests that the

Table 5. Values of synergism parameter (*S*) for different concentrations of P4VP

P4VP conc. /mg l^{-1}	*S*
1	1.18
5	1.27
15	0.98
30	1.10
100	1.22

improvement in inhibition efficiency generated by the addition of KI to P4VP is due to a synergistic effect [34].

3.3. *Electrochemical impedance spectroscopy*

Impedance diagrams obtained for frequencies ranging from 10 kHz to 20 mHz at open circuit potential for mild steel in 1 M HCl in the presence of various concentrations of P4VP alone and in combination with 0.1% KI are shown in Figures 2 and 3. These diagrams are not perfect semicircles. The difference has been attributed to frequency dispersion [35].

The fact that impedance diagrams have a semicircular appearance shows that the corrosion of steel is controlled by a charge transfer process and the presence of an inhibitor does not alter the mechanism of dissolution of steel in HCl.

Table 6 gives the values of the charge transfer resistance R_t' double layer capacitance C_{dl}' and inhibition efficiency obtained from the above plots. It can be seen that the presence of P4VP enhances the values of R_t and reduces the C_{dl} values. The decrease in C_{dl} may be due to the adsorption of P4VP to form an adherent film on the metal surface and suggests that the coverage of the metal surface with this film decreases the double layer thickness. The addition of KI further enhances R_t values and reduces C_{dl} values. This can be attributed to the enhanced adsorption of P4VP in the presence of KI because of the synergistic effect of iodide ions. Nyquist plots for mild steel in 1 M HCl in the presence of 1 mg l^{-1} P4VP in combination with 0.1% KI for different immersion times are shown in Figure 4.

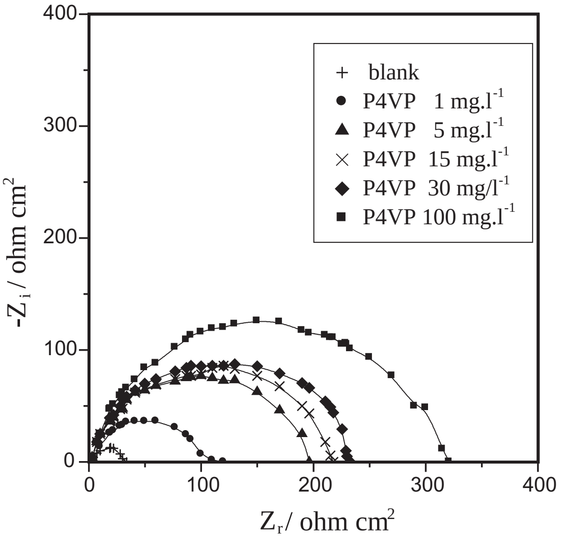

Fig. 2. Nyquist plots for mild steel in 1 M HCl containing different concentrations of P4VP.

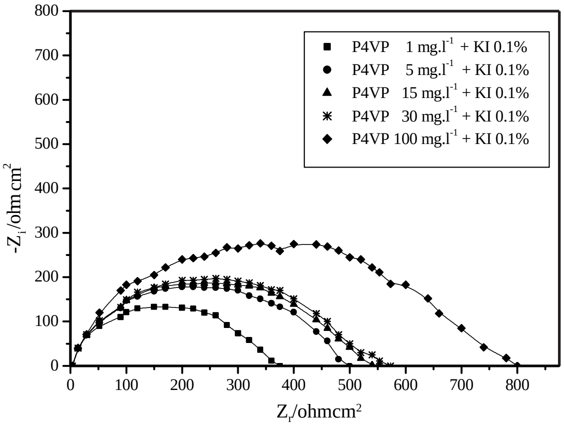

Fig. 3. Nyquist plots for mild steel in 1 M HCl containing different concentrations of P4VP in the presence of KI 0.1%.

Table 6. Impedance parameters for corrosion of mild steel in 1 M HCl with different concentrations of P4VP in the presence and absence of KI

P4VP conc. /mg l^{-1}	KI conc. /%	R_t /Ω cm^2	C_{dl} /μF cm^{-2}	*P* /%
Blank	–	30	96	–
1	–	115	75	73.91
1	0.1	374	44	91.97
5	–	197	50	84.77
5	0.1	513	38	94.15
15	–	220	41	86.36
15	0.1	523	38	94.26
30	–	228	40	86.84
30	0.1	575	37	94.78
100	–	336	38	91.07
100	0.1	792	35	96.21

Table 7 gives the values of the charge transfer resistance R_t obtained from the above plots. It is found that the R_t values for steel in 1 M HCl with the combined inhibitor (P4VP + KI) increases with immersion time.

The change in R_t values and, consequently of inhibition efficiency, may be due to the gradual replacement of water molecules by the iodide ions and by the adsorption of P4VP molecules on the metal surface, decreasing the extent of dissolution [6].

In order to correlate impedance and polarization methods, I_{corr} values were obtained from polarization curves and Nyquist plots for different concentrations of P4VP in the absence and presence of KI 0.1% using the Stern–Geary equation:

$$I_{corr} = \frac{b_a b_c}{2.3(b_a + b_c)R_t} \tag{8}$$

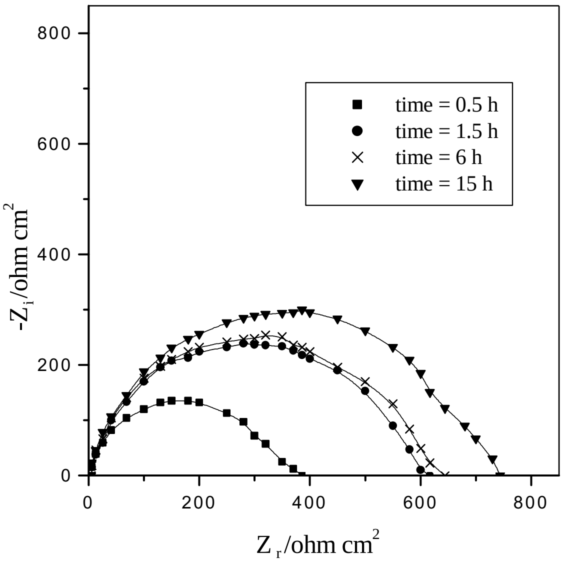

Fig. 4. Effect of immersion time on Nyquist plots of mild steel in 1 M HCl in the presence of (1 mg l^{-1} P4VP + 0.1% KI).

Table 7. Effect of immersion time on the inhibition efficiency of (P4VP mg l^{-1} + KI 0.1%) obtained from impedance measurements

Immersion time (h)	R_t (Ω cm^2)
0.5	374
1.5	600
6.0	720
15.0	704

Table 8. Values of I_{corr} and Inhibition efficiencies for corrosion of mild steel in 1 M HCl wit different concentrations of P4VP in absence and presence of 0.1% KI obtained by Stern–Geary equation

P4VP conc. /mg l^{-1}	KI conc. /%	I_{corr} /μA cm^{-2}	P /%
Blank	–	783	-
1	–	165	78.9
1	0.1	053	93.2
5	–	102	87.0
5	0.1	039	95.0
15	–	090	88.5
15	0.1	041	94.7
30	–	091	88.4
30	0.1	037	95.3
100	–	058	92.6
100	0.1	025	96.8

Table 8 gives values of I_{corr} and percentage P obtained from this equation. It can be seen that the I_{corr} values decrease significantly in the presence of P4VP and the inhibition efficiency P is greatly improved by the addition of KI. The order of reduction in I_{corr} exactly correlates with that obtained from potentiodynamic polarization studies. The maximum reduction in I_{corr} value is again observed at the P4VP concentration equal to 100 mg l^{-1}. Moreover, the decrease in the values of I_{corr} follows the same order as that obtained for the values of C_{dl}.

It can be concluded that the inhibition efficiency found from weight loss, polarization curves, electrochemical impedance spectroscopy measurements and the Stern–Geary equation are in good agreement.

3.4. *Effect of temperature*

Potentiodynamic polarization of mild steel in 1 M HCl was studied in the temperature range 25 to 55 °C in the absence and presence of different additives. The dependence of log I_{corr} on the reciprocal value of the absolute temperature for a 1 M solution of hydrochloric acid is presented in Figure 5 for a blank solution and in the presence of P4VP, KI and (P4VP + KI). Straight lines with coefficients of correlation (c.c.) in the range 0.978 – 0.995, are obtained for the supporting electrolyte and all compounds. The values of the slopes of these straight lines permit the calculation of the Arrhenius activation energy, $E^*_{a'}[\log I_{corr} = (-E^*_a/2.303\ RT) + \text{const}]$ (Table 9). The value of E^*_a obtained for 1 M HCl without an inhibitor (60.50 kJ mol^{-1}) agrees with literature data of E^*_a for iron and steel in hydrochloric acid which are in the range 58–100 kJ mol^{-1} [36–38]. The calculations show that E^*_a decreases in the presence of inhibitor.

The decrease in E^*_a in inhibited solutions and the previously considered influence of temperature on the protective effect support the assumption for chemisorption of P4VP, KI and (P4VP + KI) on the metal surface. Szauer et al. [39, 40] state that the lower activation energy value of the process in the presence of the inhibitor compared to that in its absence can be attributed to its chemisorption, while the opposite is the case with physical adsorption.

Table 10 gives values of the inhibition efficiency for the corrosion of mild steel in 1 M HCl at various temperatures in the absence and presence of 5 mg l^{-1} of different additives. The values of inhibition efficiency increase with increase in the temperature. Moreover, the

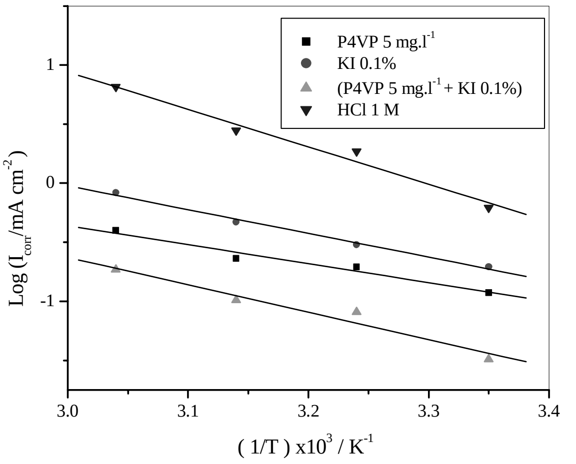

Fig. 5. log I vs. $1/T$ for mild steel dissolution in 1 M HCl in the absence and in the presence of 5 mg l^{-1} P4VP, 5 mg l^{-1} P4VP + 0.1% KI and 0.1% KI.

Table 9. Values of activation energy E_a^* for mild steel in 1 M HCl in absence and presence of additives

Sample	E_a^* /kJ mol^{-1}
HCl 1M	60.50
P4VP 5 mg l^{-1}	30.60
KI 0.1%	38.67
P4VP mg l^{-1} + KI 0.1%	44.42

Table 10. Effect of temperature on the inhibition efficiency obtained from impedance measurements

T (K)	P4VP 5 (mg l^{-1})	KI 0.1%	P4VP 5 mg l^{-1} + KI 0.1%
298	83.62	62.49	94.70
308	88.00	76.92	96.50
318	90.34	77.50	96.40
328	93.92	80.76	96.70

addition of KI enhances the inhibition efficiency of P4VP significantly at all temperatures.

The fact that P increases with increasing temperature is explained by Ammar and El Khorafi [41], as the likely specific interaction between the iron surface and the inhibitor. Ivanov [42] states that increase in P with temperature increase is due to the change in the nature of adsorption: the inhibitor is adsorbed physically at lower temperature, while chemisorption is favored as temperature increases. Other authors [43] consider this phenomenon as an increase in surface coverage by an inhibitor. Therefore, at high degrees of coverage, the diffusion of corrosion products through the surface layer containing the inhibitors becomes the rate - determining step of the metal dissolution process.

3.5. *Adsorption isotherm*

Two main types of interaction can describe the adsorption of the organic compounds: physical adsorption and chemisorption. These are influenced by the electronic structure of the metal, the type of electrolyte and the chemical structure of the inhibitor.

In order to elucidate the character of adsorption of P4VP, an adsorption isotherm describing the process was determined using the data of Table 3. The surface coverage θ of the metal surface by the adsorbed inhibitor was calculated [31] assuming no change in the mechanism of both the anodic and the cathodic reactions using the equation:

$$\theta = 1 - \frac{I'_{\mathrm{corr}}}{I_{\mathrm{corr}}} \tag{9}$$

where I'_{corr} and I_{corr} are the corrosion rates in the presence and absence of the inhibitor.

Attempts were made to fit these θ values to various isotherms including Frumkin, Langmuir, Temkin and Freundlich. By far the best fit was obtained with the Langmuir isotherm. According to this isotherm, θ is related to the inhibitor concentration C via

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{10}$$

where K designates the adsorption equilibrium constant. This equation is the ideal equation that should be applied to the ideal case of the physical and chemical adsorption on a smooth surface with no interaction between adsorbed molecules.

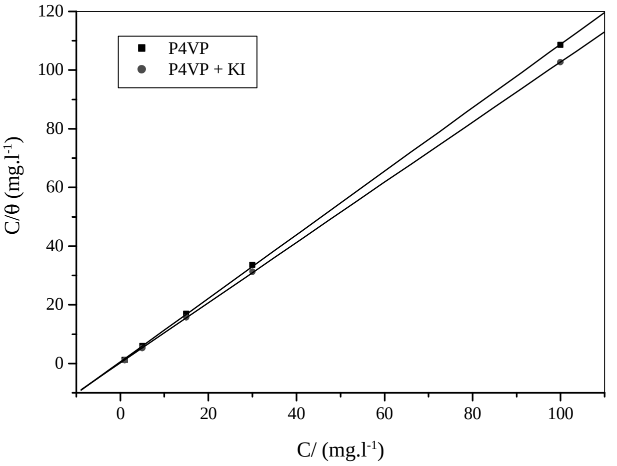

Fig. 6. Langmuir adsorption isotherm of P4VP and (P4VP + KI) on the mild steel surface in 1 M HCl from polarization measurements.

It was found that a plot of C/θ vs C gives straight lines with nearly unit slopes showing that the adsorption of P4VP alone and in combination with KI from HCl 1 M on the mild steel surface obeys the Langmuir adsorption isotherm (Figure 6).

The value of equilibrium adsorption constant obtained from the Langmuir plot is about 1.68 l mg^{-1} for P4VP and 4.35 l mg^{-1} for (P4VP + KI), suggesting a chemically adsorbed film [44]. This is in good agreement with the value of inhibition efficiency obtained from the weight loss measurements polarization curves and impedance spectroscopy.

The polarization behavior of the electrode in solution in the presence of P4VP is similar to that in the presence of (P4VP + KI). Thus the inhibitive effects of (P4VP + KI) are attributable to the adsorption of P4VP. The P4VP molecules may have stronger adsorption abilities than iodide ions, as indicated by their inhibition efficiencies.

4. Conclusion

P4VP inhibits the corrosion of mild steel in HCl and its effect is due to chemisorption of P4VP molecules on the metal surface.

P4VP affects both anodic and cathodic Tafel slopes, and is thus a mixed type inhibitor.

Synergistic effects between P4VP and KI have been observed. The addition of KI enhances the inhibition efficiency of P4VP significantly. The chemisorption of P4VP is stabilized by the presence of iodide ions in the solutions.

The adsorption of P4VP and (P4VP + KI) on the metal surface from 1 M HCl obeys the Langmuir adsorption isotherm.

The inhibition efficiency of (P4VP + KI) improves with increasing immersion time.

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