Corrosion Inhibition of Mild Steel in 1 M H₂SO₄ by Polyvinyl Pyrrolidone and Synergistic Iodide Additives

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Abstract

The corrosion inhibition of mild steel in 1M H_2SO_4 by polyvinyl pyrrolidone (PVP) and the synergistic effect of iodide ions were investigated using weight loss and hydrogen evolution methods in the temperature range of 30 – 60 °C. The corrosion rates of mild steel decreased with the increasing concentration of PVP, while the inhibition efficiency (%I) increased. The inhibition efficiency of PVP decreased with rise in temperature, suggesting a physical adsorption mechanism, which was found to follow Freundlich and Temkin adsorption isotherms. The inhibition mechanism was further collaborated by the values of kinetics/thermodynamic parameters obtained from the experimental data. The inhibiting action of PVP was considerably enhanced in the presence of iodide ions and values of the synergism parameter (S_1) obtained point to synergistic interactions between PVP and iodide ions.

Keywords: polyvinyl pyrrolidone, mild steel, synergism, corrosion inhibition, adsorption isotherm.

Introduction

Acid solutions are often used in industry for cleaning, decaling and pickling of steel structures, processes which are normally accompanied by considerable dissolution of the metal. A useful method to protect metals deployed in service in such aggressive environments against corrosion is the addition of species to the solution in contact with the surface in order to inhibit the corrosion reaction and reduce the corrosion rate. A number of organic compounds [1-8] are known to be applicable as corrosion inhibitors for steel in acidic environments. Such compounds typically contain nitrogen, oxygen or sulphur in a conjugated system

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and function via adsorption of the molecules on the metal surface, creating a barrier to corrodent attack. To further upgrade the performance of such organic inhibitors, extensive studies have been undertaken to identify synergistic effects of other additives. Interestingly, addition of halide ions to sulphuric acid solutions containing some organic compounds has been reported to yield the required enhancement [1-13]. The inhibitive effects for the halides have been observed to increase in the order $Cl^- < Br^- < I^-$, with the iodide ion being the most effective. It is thought that the initial specific adsorption of the halide ions on the metal surface facilitates the adsorption of organic cations by forming intermediate bridges between the positively charged metal surface and the positive end of the inhibitor.

A few reports from our laboratory highlighted the synergistic effect of halide ions on the corrosion of mild steel in acidic solution [15-17], while the synergistic inhibition between organic compounds and iodide ions has been reported by some research groups [18-22]. However, reports on synergistic influence of halide ions and polymers are very scanty [23, 24]. As part of our contribution to the growing interest of exploring polymeric materials as corrosion inhibitors, the present study investigates the inhibitive effect of polyvinyl pyrrolidone on mild steel corrosion in sulphuric acid, including the synergistic effect of iodide ions using weight loss and hydrogen evolution methods in the temperature range $30 - 60\ ^oC$.

Experimental
Materials preparation
The composition and preparation of the metal are as previously reported [16,17,25]. The aggressive solution was 1.0 M H_2SO_4 solution, prepared from analytical reagent grade concentrated acid using double distilled water. Polyvinyl pyrrolidone (PVP, Hi-Tek polymers, Japan) [M_n = 44,000 $gmol^{-1}$], with the repeat unit shown below, was used as inhibitor in the concentration range $2x10^{-5}$ to $1x10^{-4}$ M. Potassium iodide (KI, BDH) was used in the concentration range 0.02 to 0.10 M. For systems containing PVP + KI, a fixed concentration of KI (0.06 M) was employed while the PVP concentration was varied.
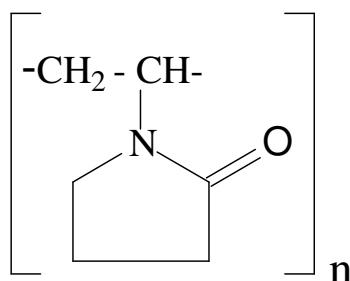
Weight loss measurements
Gravimetric experiments were conducted under total immersion conditions in 250 mL of test solutions maintained at $30 - 60\ ^oC$. All tests were made in aerated solutions. Test coupons were retrieved at 24 h intervals progressively for 7 days,

immersed in 20% NaOH containing 200 gL^{-1} zinc dust, scrubbed with a bristle brush, washed, dried and reweighed. The weight loss was taken as the difference between the weight at a given time and the initial weight of the coupons. The inhibition efficiency (%I) and the surface coverage (θ) of the inhibitor were evaluated from equations (1) and (2), respectively:

$$Inhibition\ efficiency\ I(\%) = \left(1 - \frac{W_i}{W_o}\right) x\,100 \qquad (1)$$

$$Surface\ coverage,\ \theta = 1 - \frac{W_i}{W_o} \qquad (2)$$

where W_i and W_o are the corrosion rates for mild steel in the presence and absence respectively, of the inhibitors. The corrosion rate was determined for a 168 h immersion period as follows:

$$Corrosion\ rate\ (mpy) = \frac{534W}{\rho At} \qquad (3)$$

where W is the weight loss (g), ρ is the density of the specimen (gcm^{-3}), A is the area of the specimen (cm^2), and t is the exposure time (h).

Hydrogen evolution measurements
The procedure adopted for this technique was as previously reported [16, 17, 26, 27]. The test solution was kept at 100 mL. The progress of corrosion reaction was monitored by careful measurement of the volume of hydrogen gas evolved at fixed time intervals.
The inhibition efficiency (%I) and degree of surface coverage were obtained from:

$$Inhibition\ efficiency\ I(\%) = \left(1 - \frac{V_{Ht}^1}{V_{Ht}^o}\right) x\,100 \qquad (4)$$

$$Surface\ coverage\ (\theta)\ = \theta = 1 - \frac{V_{Ht}^1}{V_{Ht}^o} \qquad (5)$$

where V_{Ht}^1 and V_{Ht}^o are the volumes of H_2 evolved at time 't' for inhibited and uninhibited solutions, respectively.

Results and discussion
Weight loss measurements
The effect of different inhibitor systems PVP, KI and PVP-KI on the corrosion of mild steel in H_2SO_4 solution was studied using the weight loss technique at 30 - 60 ^{o}C. Fig. 1 shows the weight loss - time curves obtained in the absence and presence of $1x10^{-4}$ M PVP, 0.06 M KI and $1x10^{-4}$ M PVP + 0.06 M KI at 30 ^{o}C.
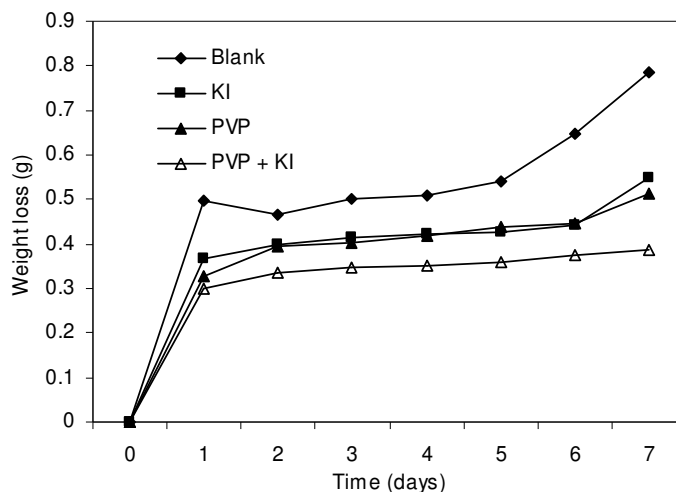
Figure 1. Weight loss-time curves for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of KI, PVP and PVP + KI at 30 ^oC.

Similar relationships were obtained at 40, 50 and 60 ^oC. The results show that the weight loss was reduced in the presence of all the additives, indicating corrosion inhibition. The PVP + KI system exhibited the greatest inhibiting effect, while PVP and KI, separately, displayed comparable effects. Calculated values of corrosion rate and inhibition efficiency (%I) for the different systems presented in Table 1 also show a reduction in corrosion rate in the presence of the additives compared to the blank, and this effect was more pronounced with increasing PVP concentration.

Table 1. Calculated values of corrosion rate (mpy) and inhibition efficiency (%I) for mild steel corrosion in 1 M H_2SO_4 for different systems at 30-60 ^oC from weight loss measurements.

Systems/concentration	Corrosion rate (mpy) x10^{-3}				Inhibition efficiency (%I)			
	30 ^oC	40 ^oC	50 ^oC	60 ^oC	30 ^oC	40 ^oC	50 ^oC	60 ^oC
Blank	8.74	11.03	13.11	15.73	-	-	-	-
0.06 M KI	3.06	4.59	6.12	9.41	64.9	58.40	53.30	40.17
2x10^{-5} M PVP	4.18	6.27	8.36	11.74	52.17	43.25	36.23	25.37
4x10^{-5} M PVP	3.89	5.84	7.79	10.72	55.49	47.05	40.58	31.66
6x10^{-5} M PVP	3.56	5.34	7.12	9.89	59.27	51.58	45.69	37.13
8x10^{-5} M PVP	3.26	4.89	6.51	9.52	62.70	55.67	50.34	39.48
1x10^{-4} M PVP	2.87	4.31	5.74	8.34	67.16	60.92	56.22	46.98
2x10^{-5} M PVP+0.06 M KI	2.72	4.08	5.44	7.85	68.88	63.01	58.50	50.09
4x10^{-5} M PVP+0.06 M KI	2.45	3.68	4.90	7.26	71.96	66.64	62.62	53.84
6x10^{-5} M PVP+0.06 M KI	2.20	3.30	4.40	6.92	74.83	70.08	66.44	56.01
8x10^{-5} M PVP+0.06 M KI	1.53	2.75	3.66	6.18	79.06	75.06	72.08	60.71
1x10^{-4} M PVP+0.06 M KI	1.72	2.58	3.44	5.60	80.32	76.61	73.76	64.39

The inhibitive effect of PVP was further improved upon addition of iodide ions suggesting cooperative effect. Table 1 also shows corresponding increase in inhibition efficiency with increasing PVP concentration as well as on introduction of KI to PVP, with the optimum value of 80.32% obtained with $1x10^{-4}$ M PVP + KI. Inhibition efficiency is also observed to generally decrease with rise in temperature, suggesting that metal/inhibitor interactions become less as the system temperature is raised from 30 through 60 ^{o}C.

Hydrogen evolution measurements

Experiments were also undertaken using the gas-volumetric technique. This technique, apart from its experimental rapidity, ensures a more sensitive monitoring in situ of any perturbation by an inhibitor vis-à-vis gas evolution on the metal-corrodent surface. This assertion has been firmly established in earlier reports [29-33]. The corrosion rates of mild steel in the absence and presence of the additives were assessed by monitoring the volume of hydrogen gas evolved at fixed time intervals. Fig. 2 shows representative plots of the volume of the hydrogen gas evolved as a function of reaction time at 30 ^{o}C. Similar plots were obtained at 40, 50 and 60 ^{o}C. It is observed from the figure that the volume of hydrogen gas evolved varies linearly with time and was less in the presence of PVP and iodide ions compared to the free acid solution. Further reduction in the volume of hydrogen gas evolved is noticed on the introduction of iodide ions to inhibited solutions containing PVP.
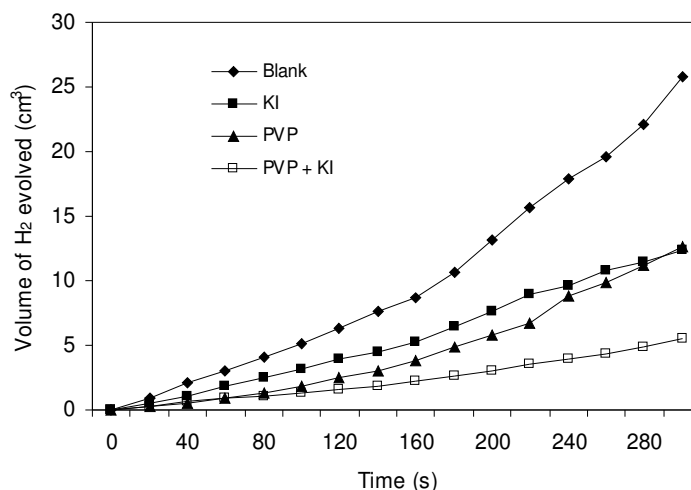

Figure 2. Volume of H_2 evolved with time for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of KI, PVP and PVP + KI at 30 ^{o}C.

Table 2 shows the calculated values of corrosion rate (mLs^{-1}) and inhibition efficiency (%I) for the different test solutions as determined using the gasometric technique. The data presented in the table follow the same trend observed for weight loss method. Corrosion rate decreased in the presence of the additives (KI, PVP and PVP+KI) and increased with rise in temperature. Inhibition

efficiency decreased with rise in temperature and increased with increase in concentration of PVP. The differences in actual values for the two methods can be attributed to the difference in time required to form an adsorbed layer of the inhibitor on the metal surface.

Table 2. Calculated values of corrosion rate (mLs^{-1}) and inhibition efficiency (%I) for mild steel corrosion in 1 M H$_2$SO$_4$ for different systems at 30-60 ^{o}C from hydrogen evolution measurements.

Systems/concentration	Corrosion rate (mLs^{-1}) x10^{-3}				Inhibition efficiency (%I)			
	30 ^{o}C	40 ^{o}C	50 ^{o}C	60 ^{o}C	30 ^{o}C	40 ^{o}C	50 ^{o}C	60 ^{o}C
Blank	4.30	5.07	6.60	8.23	-	-	-	-
0.06 M KI	2.07	2.72	3.80	6.53	51.94	46.38	42.42	20.81
2x10^{-5} M PVP	3.47	4.20	5.73	7.33	19.40	17.11	13.13	11.11
4x10^{-5} M PVP	2.82	3.70	5.05	6.95	34.50	26.97	23.48	15.76
6x10^{-5} M PVP	2.62	3.33	4.45	5.63	39.15	34.21	32.48	31.72
8x10^{-5} M PVP	2.27	3.08	4.08	5.43	47.30	39.14	38.13	34.14
1x10^{-4} M PVP	2.10	2.83	3.97	5.17	51.16	44.08	39.97	37.37
2x10^{-5} M PVP+0.06 M KI	1.78	3.35	4.87	6.48	58.53	33.88	26.26	21.41
4x10^{-5} M PVP+0.06 M KI	1.53	2.83	3.98	5.52	64.34	44.08	39.64	33.13
6x10^{-5} M PVP+0.06 M KI	1.45	2.58	3.50	4.95	66.30	49.01	46.97	40.00
8x10^{-5} M PVP+0.06 M KI	1.18	2.33	3.17	4.33	72.48	53.95	52.02	47.47
1x10^{-4} M PVP+0.06 M KI	0.92	1.78	2.87	3.92	78.68	64.80	56.57	52.53

Adsorption considerations

The inhibition of mild steel corrosion in the presence of the various organic additives has been attributed to their adsorption onto the metal surface and this is usually confirmed from the fit of the experimental data to various adsorption isotherms. The adsorption process is influenced by the nature and surface charge of the metal, by the type of aggressive electrolyte and by the chemical structure of the inhibitors [34, 35]. The gravimetric data from the present study were fitted to the most frequently used adsorption isotherms, namely: Temkin, Frumkin, Langmuir, Freundlich, Hill de Boer, Parsons, Flory Huggins, Dhar-Flory Huggins, and Bockris Swinkles, and the correlation coefficients (R^2) were used to determine the best fits. All of these isotherms are of the general form [36]

$$f(\theta, x)\exp(-2a\theta) = KC \qquad (6)$$

where f (θ, x) is the configurational factor which depends upon the physical model and assumption underlying the derivative of the isotherm [36], θ is the surface coverage, C is the inhibitor concentration, x is the size ration, 'a' is the molecular interaction parameter and K is the equilibrium constant of adsorption process. The Freundlich and Temkin adsorption isotherms were found to best

describe the experimental results for PVP as well as PVP + KI adsorption on the corroding steel surface at the temperature range studied, with R^2 ranging from 0.94 to 0.99. Fig. 3 shows the plot of logarithm of inhibition efficiency versus logarithmic concentration of additives (a) PVP and (b) PVP + KI at different temperatures. Straight lines were obtained indicating that the adsorption of the additives onto mild steel surface can be approximated by Freundlich isotherm.
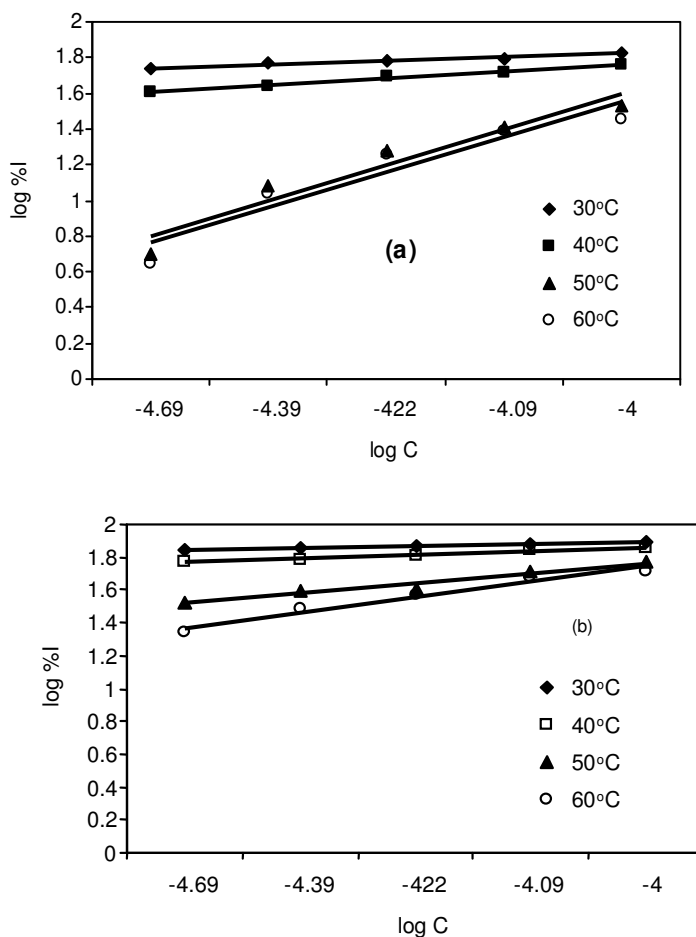

Figure 3. Freundlich adsorption isotherm plot for mild steel corrosion in 1 M H_2SO_4 in the presence of (a) PVP and (b) PVP + KI at 30 – 60 ^{o}C.

Fig 4 shows the plot of surface coverage (θ) as a function of logarithm of inhibitor concentration (log C) for mild steel in 1 M H_2SO_4 containing (a) PVP and (b) PVP + KI at different temperatures. Linear plots were again obtained, which shows that Temkin adsorption isotherm is obeyed. The characteristics of Temkin isotherm are given by the equation:

$$\exp(-2a\theta) = KC \qquad (7)$$

The adsorption parameters deduced from Temkin isotherm are presented in Table 3. It is also seen that the values of 'a' are negative in all cases, indicating that repulsion exists in the adsorption layer [37]. It is generally known that K denotes the strength between the adsorbate and adsorbent. Large values of K imply more efficient adsorption and hence better inhibition efficiency [34]. K values, as shown in Table 3, are in the order (PVP +KI) > PVP.

The fit of experimental data to the above isotherms suggests that the additives inhibit the corrosion reaction by adsorption on the metal surface. The additives could be adsorbed by the interaction between the lone pair of the electrons of the oxygen and nitrogen atoms respectively on the polyvinyl pyrrolidone moiety and metal surface (chemical adsorption). Moreover PVP should be protonated at the N atom in the acidic solution and can interact with the metal surface through electrostatic attraction (physical adsorption) [23, 24].
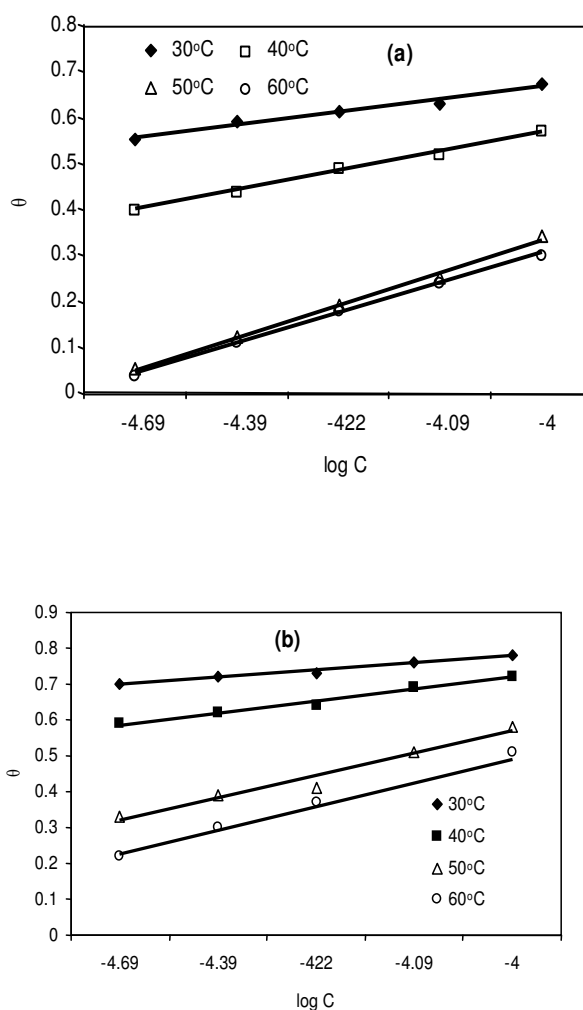

Figure 4. Temkin adsorption isotherm plot for mild steel corrosion in 1 M H_2SO_4 in the presence of (a) PVP and (b) PVP + KI at 30 - 60 ^oC.

The decrease in inhibition efficiency with rise in temperature, as illustrated in Tables 1 and 2, suggests possible desorption of some of the adsorbed inhibitor from the metal surface at higher temperatures. Such behavior shows that the

additives were physically adsorbed on the metal surface [4, 12]. This is further confirmed by the decrease in K values with rise in temperature, as seen in Table 3. The proposed physisorption mechanism may be rationalized by considering the fact that the PVP could interact with the corroding steel surface via the protonated N atom, which can be adsorbed at cathodic sites and hinder the hydrogen evolution reaction, with possible contributions from the lone pair of the electrons on the oxygen atom.

Table 3. Some parameters of the linear regression from Temkin adsorption isotherm.

Inhibitor	Temperature (^{o}C)	Temkin isotherm			
		ΔG (kJ/mol)	a	K	R^2
	30	-20.09	-7.75	5.98×10^{18}	0.95
PVP	40	-19.84	-5.17	3.35×10^8	0.99
	50	-14.47	-3.06	0.47	0.99
	60	-14.69	-2.82	0.53	0.99
	30	-20.77	-10.86	9.21×10^{33}	0.95
PVP+KI	40	-21.55	-6.58	5.75×10^{16}	0.95
	50	-19.75	-3.50	1.44×10^4	0.96
	60	-19.21	-3.29	2.47×10^2	0.94

The increase in inhibition efficiency of PVP in the presence of KI results from initial specific adsorption of iodide ions on the steel surface, thereby increasing the negative charge on the metal surface, which then facilitates adsorption of protonated PVP, leading to improved surface coverage, hence higher inhibition efficiency.

Kinetics/thermodynamics studies

The apparent activation energy E_a for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of inhibitors was evaluated from Arrhenius equation:

$$LogCR = LogA - \frac{E_a}{2.303RT} \qquad (8)$$

where CR is the corrosion rate determined from gravimetric measurements, A is the Arrhenius frequency factor, R is the molar gas constant and T is the absolute temperature. The plots of log CR against 1/T were linear, as shown in Fig.5. E_a values were obtained from the slope and are as presented in Table 4. E_a values were found to be higher in the presence of the additives compared to the free acid solution. This further support the earlier suggestion that PVP alone and in combination with iodide ions were physically adsorbed onto the mild steel surface.
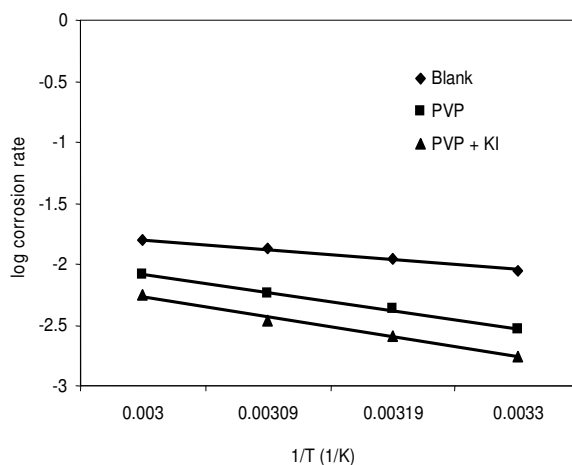
Figure 5. Arrhenius plot for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of KI, PVP and (PVP + KI).

Table 4. Activation energy for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of PVP and (PVP+KI).

Systems/concentrations	Activation energy, E_a (kJ/mol)
Blank	16.5
1×10^{-4} M PVP	28.7
1×10^{-4} M PVP + 0.06 M KI	31.8

The free energy of adsorption ΔG^o_{ads} values were obtained from the intercept of Freundlich adsorption isotherm plot (Fig. 3) and evaluated using the following expression [38, 39]:

$$LogC = Log\left(\frac{\theta}{1-\theta}\right) - LogB \qquad (9)$$

where log B = -1.74 – (ΔG^o_{ads}/2.303RT) and C is the concentration of the systems studied. The values of ΔG^o_{ads} at the temperature range studied are presented in Table 3. The negative values of ΔG^o_{ads} suggest spontaneous adsorption of the inhibitor and usually characterize their strong interaction with the metal surface.
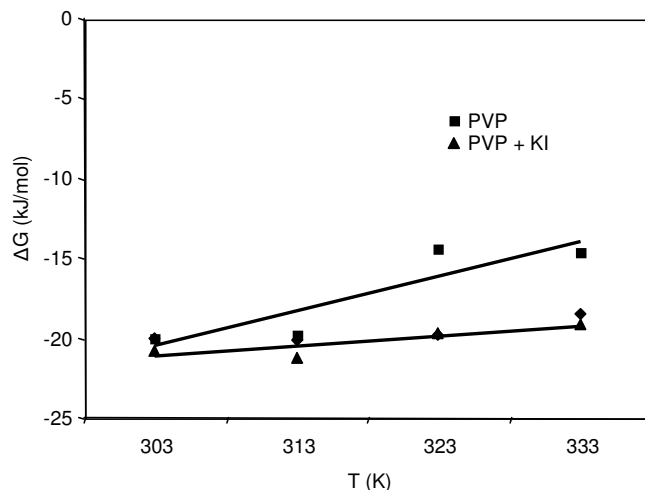
Figure 6. Plot of free energy of adsorption against temperature for mild steel corrosion in 1 M H_2SO_4 in the presence PVP and (PVP + KI).

Generally, values of ΔG^o_{ads} up to -20 kJ/mol (as obtained in this study) are consistent with electrostatic interactions between the charged molecules and the charged metal surface, which indicates physical adsorption [27, 38, 39]. Other thermodynamic functions, namely enthalpy of adsorption, ΔH^o_{ads}, and entropy of adsorption, ΔS^o_{ads}, were obtained from intercept and slope, respectively, of the plot of ΔG^o_{ads} against T depicted in Fig. 6 according to the relationship:

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \qquad (10)$$

The enthalpy of adsorption, ΔH^o_{ads} values were -22.66 kJ/mol and -21.78 kJ/mol for PA and (PA+KI), respectively, while the entropy of adsorption, ΔS^o_{ads} values were 2.16 kJ $mol^{-1}K^{-1}$, and 0.62 kJ $mol^{-1}K^{-1}$, respectively. The negative values of ΔH^o_{ads} indicate that adsorption process was spontaneous, while the positive values of ΔS^o_{ads} show a decrease in the systems order [40]. The values of ΔH^o_{ads} obtained in this study are low (between -20.86 kJ/mol and -22.66 kJ/mol) confirming that the inhibitors were physically adsorbed onto the mild steel surface, since ΔH^o_{ads} of absolute values lower than 41.86 kJ/mol indicate physical adsorption, and values approaching 100 kJ/mol indicate chemical adsorption [41].

Synergism considerations
The synergism parameter S_1 was evaluated using the relationship given initially by Aramaki and Hackerman [42]:

$$S_1 = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \qquad (11)$$

where $I_{1+2} = (I_1 + I_2)$; I_1 is the inhibition efficiency of the iodide ion, I_2 is the inhibition efficiency of PVP and I'_{1+2} is the inhibition efficiency of PVP in

combination with iodide ion. S_1 approaches unity when there are no interactions between the inhibitor compounds, while $S_1 > 1$ points to a synergistic effect; in the case of $S_1 < 1$, the antagonistic interaction prevails, which may be attributed to competitive adsorption. The values of the synergism parameter for the various concentrations of PVP studied were calculated from the gravimetric data at 30 and the results are presented in Table 5. Values shown in this table are all greater than unity. This is an indication that the enhanced inhibition efficiency resulting from the addition of iodide ions to PVP is synergistic in nature. Similar observation has been reported by Larabi and Harek [24] and Larabi *et al.* [25] in their study of addition of iodide ions to poly (4-vinylpyridine) (P4VP) in 0.5 M H_2SO_4 and 1 M HCl, respectively. This can be explained on the basis that halide ions have a greater tendency to be adsorbed on the surface, and this could be responsible for the synergistic effect of iodide ions in combination with PVP. It is thought that the halide ions are able to improve adsorption of the organic cations

Table 5. Synergism parameter (S_1) for different concentrations of PVP in combination with 0.6 M KI.

Concentration of PVP	Synergism parameter, S_I
2×10^{-5} M	1.72
4×10^{-5} M	1.68
6×10^{-5} M	1.67
8×10^{-5} M	1.62
1×10^{-4} M	1.65

by forming intermediate bridges between the positive charged metal surface and the positive end of the organic inhibitor. Corrosion inhibition synergism thus results from the increased surface coverage arising from the ion-pair interactions between the organic inhibitor and halide ions. According to Fishtik [43], two possible mechanisms account for the adsorption of such ion pairs on the metal surface. On one mechanism, the ion pairs are formed in the bulk of the solution and then adsorbed from the solution onto the metal surface as follows:

$$Y_s + X_s \rightarrow (YX)_s \tag{12}$$

$$(YX)_s \rightarrow (YX)_{ads} \tag{13}$$

In the second mechanism, the halide ions are first adsorbed on the metal surface and the inhibitor is then drawn into the double layer by the adsorbed halide ion, such that the ion pair formation occurs directly on the metal surface:

$$X_s \rightarrow X_{ads} \tag{14}$$

$$Y_s + X_{ads} \rightarrow (YX)_{ads} \tag{15}$$

where Y_s, X_s and $(YX)_s$ represent inhibitor, halide ion and ion-pair, respectively, in the bulk solution, while Y_{ads}, X_{ads} and $(YX)_{ads}$ refer to the same species in the adsorbed state.

Conclusions

On the basis of the experimental results obtained in the present study, the following conclusions can be drawn.

1. PVP acts as an inhibitor for mild steel corrosion in acidic medium.
2. Inhibition efficiency increases with increase in concentration of PVP and decreases with rise in temperature.
3. The addition of iodide ions to PVP enhanced the inhibition efficiency due to synergistic effect.
4. The adsorption of PVP alone and in combination with iodide ions obeys Freundlich and Temkin adsorption isotherms.
5. Experimental results obtained indicate that adsorption of PVP and PVP +KI onto mild steel surface is spontaneous.

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