

Synergistic Inhibition Effect of Polyethylene Glycol–Polyvinyl Pyrrolidone Blends for Mild Steel Corrosion in Sulphuric Acid Medium

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ABSTRACT: The corrosion inhibition of mild steel in sulphuric acid solution in the presence of polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP), and their blends was investigated using weight loss and hydrogen evolution techniques at temperature range of 30–60°C. It was found that inhibition efficiency ($\eta\%$) increases with increase in concentration of the homopolymers and decreases with increase in temperature. Inhibition efficiency was found to be synergistically enhanced on blending the two polymers with highest inhibition efficiency

obtained for (PEG : PVP) blending ratio of 1 : 3. The experimental data obtained fitted well into Temkin adsorption isotherm model. Physical adsorption mechanism is proposed from the trend of inhibition efficiency with temperature. The proposed mechanism is also corroborated by kinetic and thermodynamic parameters obtained. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2072–2084, 2011

Key words: polyvinyl pyrrolidone; polyethylene glycol; polymer blends; synergism; mild steel; corrosion inhibition

INTRODUCTION

The use of inhibitors is one of the most practical methods for protecting metals against corrosion and it is becoming increasingly popular. Most of the well known acid inhibitors are organic compounds containing nitrogen, sulphur, phosphorous, and oxygen atoms. The efficiency of these molecules is mainly dependent on their ability to get adsorbed on the metal surface with the polar groups acting as the reactive centers resulting in the replacement of water molecules at the corroding interface.^{1,2} To further improve the performance of organic corrosion inhibitors, extensive studies have been undertaken to identify synergistic effects of other additives. Combination of organic compounds with certain metal cations such as Cu^{2+} , As^{3+} , Sb^{3+} , Sn^{2+} , Zn^{2+} , Mg^{2+} , La^{3+} , etc.^{3–7} and halide anions namely Cl^- , Br^- , and I^- ^{8–12} have been reported to yield the required enhancements. However, the use of heavy metal-based corrosion inhibitors is increasingly being curtailed by recent environmental restrictions. As a result, the current trend for inhibitors use is to employ mixtures of organic inhibitors. The synergistic inhibition effect of combination of two organic inhibitors can be found in the literature. For

instance, Villamil et al.¹³ reported a synergistic corrosion inhibition effect between sodium dodecylsulphate and benzotriazole for copper in sulphuric acid solution. Ramji et al.¹⁴ reported that inhibition efficiency of 79.0 and 62.5% were obtained in the presence of optimum concentration of 2-mercaptobenzothiazole (MBT) and polyoxyethylene sorbitan monooleate (Tween-80), respectively, for brass in 0.2 M NaCl solution. The addition of the mixture of MBT and Tween-80 synergistically enhanced the inhibition efficiency to 94.0%. Also reported is the synergistic inhibition behavior between sodium dodecylbenzenesulphonate (SDBS) and 2-mercaptobenzoxazole (2-MBO) for copper in 0.5 M H_2SO_4 solution.¹⁵ Lalitha et al.¹⁶ studied the effect of combination of triazoles and surfactants on the control of corrosion of copper in acidic solution and the results indicated that a marked synergism effect was shown by all the combinations of triazole and surfactant. The effect of ethylenediamine tetraacetic acid disodium (EDTA) on the corrosion of cold rolled steel in the presence of benzotriazole (BTA) in 0.1 M HCl has been reported by Qu et al.¹⁷ It was found that combination of EDTA and BTA showed strong synergism effects at 30 and 40°C. The synergistic inhibition effect of sodium octylmercaptopropionate (SOMP) and 8-quinolinol (QI) on the corrosion of iron in an aerated 0.5 M Na_2SO_4 solution has been reported by Suzuki et al.¹⁸ A high inhibition efficiency of 98.2% was obtained by a mixture of 3×10^{-4} M SOMP and 5×10^{-4} M QI. Synergistic effect of benzoate and benzotriazole on passivation of mild

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steel has also been reported.¹⁹ The inhibition effects of sodium dodecylbenzenesulphonate (SDBS) and hexamethylenetetramine (HA) on the corrosion of mild steel in sulphuric acid solution was studied by Hosseini et al.²⁰ Results obtained showed that on mixing SDBS and HA, a slight antagonistic effect was observed if one of the additives is present in a concentration below 75 ppm while at higher concentrations, a moderate synergism was found.

The use of polymers as corrosion inhibitors has attracted attention and has gained wide acceptance in recent times. This has been attributed to a number of factors namely: (i) they are low cost and stable to metallic materials in acid media, (ii) they possess multiple adsorption sites, (iii) through their functional groups, they form complexes with metal ions and on the metal surface these complexes occupy a large area, thereby blanketing the surface and protecting the metal from corrosive agents present in the solution.^{21–23} A number of polymers including polyethylene glycol and polyvinyl pyrrolidone have been reported to inhibit the corrosion mild steel in acidic media.^{24–28} In some cases, their inhibition efficiency has been upgraded by addition of small amount of cations or anions which functioned by exerting synergistic action.^{29–34} However, reports on the effect of polymer–polymer mixtures or blends on corrosion inhibition of metals is very scarce.^{35,36} We have reported in our laboratory the corrosion inhibition of aluminium in 0.1 M HCl using polyacrylamide (PA) and polyvinyl pyrrolidone (PVP) blend.³⁷ It was found that the inhibition efficiency was enhanced on blending the two polymers with the optimum inhibition efficiency obtained at blending ratio of 3 : 1 for PVP : PA at 30°C. To extend the investigation to other service conditions, the present study reports on the corrosion and corrosion inhibition effect of polyethylene glycol (PEG) and polyvinyl pyrrolidone (PVP) solution blends for mild steel in H₂SO₄ using weight loss and hydrogen evolution techniques at 30–60°C.

EXPERIMENTAL

Materials

Mild steel sheets of composition M_n 0.6%, C 0.15%, P 0.03%, and remaining Fe were used in the study. Each sheet of 0.046 cm thickness was mechanically pressed cut into coupons of dimensions 5 cm × 4 cm (for weight loss studies) and 3 cm × 3 cm × 0.046 cm (for hydrogen evolution studies). These coupons were used without further polishing to ensure reproducible surface. However, they were degreased in absolute ethanol, dried in acetone, and stored in a moisture free dessicator prior to use in corrosion studies. The inhibitors, polyethylene gly-

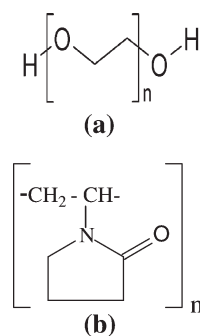


Figure 1 Chemical structures of (a) PEG and (b) PVP repeat unit.

col (PEG) [$M_n = 10,000$ g/mol, BDH] and polyvinyl pyrrolidone (PVP) [$M_n = 44,000$ g/mol, product of Hi-Tek polymers, Japan] with chemical structure of the repeat units shown in Figure 1 were used as obtained in the concentration range 1×10^{-5} to 1×10^{-4} M. The concentration of 1×10^{-4} M of each of the polymers was used to evaluate the effect of the blends. PEG and PVP were blended in the ratios 1 : 1, 1 : 2, 1 : 3, 2 : 1, and 3 : 1 (v/v). The corrosive medium was 0.5 and 1 M H₂SO₄ for weight loss and hydrogen evolution measurements, respectively, prepared from 98% analytical grade supplied by BDH. Double distilled water was used for the preparation of all reagents.

Weight loss measurements

Weight loss measurements was conducted in a glass reaction vessels containing 150 mL of test solution maintained at 30–60°C. Tests were performed under total immersion in the absence and presence of the inhibitors. In each experiment, the cleaned and weighed mild steel coupon was suspended in the different test solutions in a beaker with the help of glass rod and hook. The test coupons were retrieved at 24 h interval progressively for 7 days (168 h), washed thoroughly in 20% NaOH solution containing 200 g/L of zinc dust,³⁸ scrubbed with bristle brush, washed in running water, and dried in acetone and weighed. The weight loss was taken as the difference between the weight at a given time and the initial weight of the coupon. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of the weight loss is reported. The reproducibility of the experiment was higher than 95%. From the weight loss values, corrosion rates were computed using the expression:

$$\text{CR (mm/yr)} = \frac{87.6W}{\rho A t} \quad (1)$$

where CR is the corrosion rate, W is the weight loss of the mild steel coupon after 168 h of immersion

(mg), ρ is the density of mild steel specimen (g cm^{-2}), A is the area of the mild steel coupon (cm^2), and t is the exposure time (h).

The inhibition efficiency of PEG, PVP, and their blends was evaluated from eq. (2):

$$\% \eta = \left(\frac{\text{CR}_{\text{blank}} - \text{CR}_{\text{inh}}}{\text{CR}_{\text{blank}}} \right) \times 100 \quad (2)$$

where CR_{blank} and CR_{inh} are the corrosion rates of the mild steel coupons in the absence and presence of additives, respectively, in 0.5 M H_2SO_4 at the same temperature.

Hydrogen evolution measurements

The technique relies on measurement of the volume of hydrogen gas evolved from the surface of a corroding metal. The measurement was performed using gasometric assembly. The detailed description of the gasometric assembly has been given in earlier report.³⁹ The procedure followed has been described elsewhere.^{24,31–33} The test solution was kept at 100 mL. The progress of corrosion in the absence of test inhibitors was monitored by careful measurements of the volume of hydrogen gas evolved at fixed time intervals. The experiments were performed for 1 M H_2SO_4 (blank), different concentrations of inhibitors ($1 \times 10^{-5} - 1 \times 10^{-4}$) and different PEG-PVP blending ratios at 30–60°C maintained using a thermostated water bath. The inhibition efficiency ($\eta\%$) was calculated using the equation:

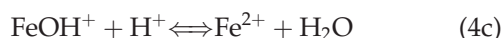
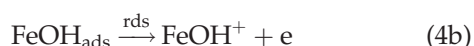
$$\eta\% = \left(1 - \frac{V_{\text{H}_2}^1}{V_{\text{H}_2}^0} \right) \times 100 \quad (3)$$

where $V_{\text{H}_2}^1$ is the volume of hydrogen evolved at time 't' for inhibited solution and $V_{\text{H}_2}^0$ is the volume of hydrogen evolved at time 't' for uninhibited solution.

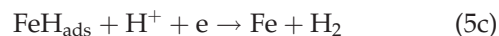
RESULTS AND DISCUSSION

Inhibition by PEG and PVP

The anodic dissolution of iron in acidic solutions has been reported to proceed according to the mechanism^{40,41}:



The accompanied cathodic hydrogen evolution reaction follows the steps:



As a consequence of these reactions, including the high solubility of the corrosion product, the metal losses weight in the solution. The corrosion of mild steel in H_2SO_4 solution and its inhibition on introduction of PEG and PVP into the corrosive medium was therefore assessed using weight loss and hydrogen evolution measurements. Corrosion inhibition is thought to be initiated by the displacement of adsorbed water molecules by the inhibitor species leading to the specific adsorption of the inhibitor on the metal surface.^{42,43} Figure 2 shows the plot of inhibition efficiency against inhibitor concentration for (a) PEG and (b) PVP at different temperatures from the weight loss measurements. A similar plot from hydrogen evolution measurements is depicted in Figure 3 for (a) PEG and (b) PVP. Examination of the plots revealed that inhibition efficiency increases with increase in concentration of the tested compounds. This suggests that more inhibitor molecules were adsorbed on the metal surface at higher concentration, leading to greater surface coverage. Also inhibition efficiency is observed to decrease with increase in temperature from the two techniques employed. This suggests a possible shift of the adsorption–desorption equilibrium towards desorption of adsorbed inhibitor. In addition, the boost in solution agitation resulting from higher rates of hydrogen gas evolution as well as roughening of the metal surface as a result of enhanced corrosion may also reduce the ability of the inhibitor to be adsorbed on the metal surface at elevated temperatures.^{44,45} According to some authors,^{46–48} a decrease in inhibition efficiency with rise in temperature suggests that inhibitor molecules are physically adsorbed on the metal surface while the reverse suggests chemical adsorption of the inhibitor molecules. The trend of inhibition efficiency with temperature as shown in Figures 2 and 3 suggests that both PEG and PVP molecules were physically adsorbed on mild steel surface.

Results from the weight loss measurements show that at the highest concentration (1×10^{-4} M) of the inhibitors studied and at 30°C, the inhibition efficiency for PEG and PVP obtained were 60 and 67%, respectively. This indicates that PVP is a better inhibitor than PEG within the range of experimental conditions in this present study. Although the corrosion inhibition mechanism seems to be the same for the two inhibitors, the differences in inhibition efficiency could be attributed to their differences in molecular structures. The relationship between inhibitor molecular structures and their inhibiting

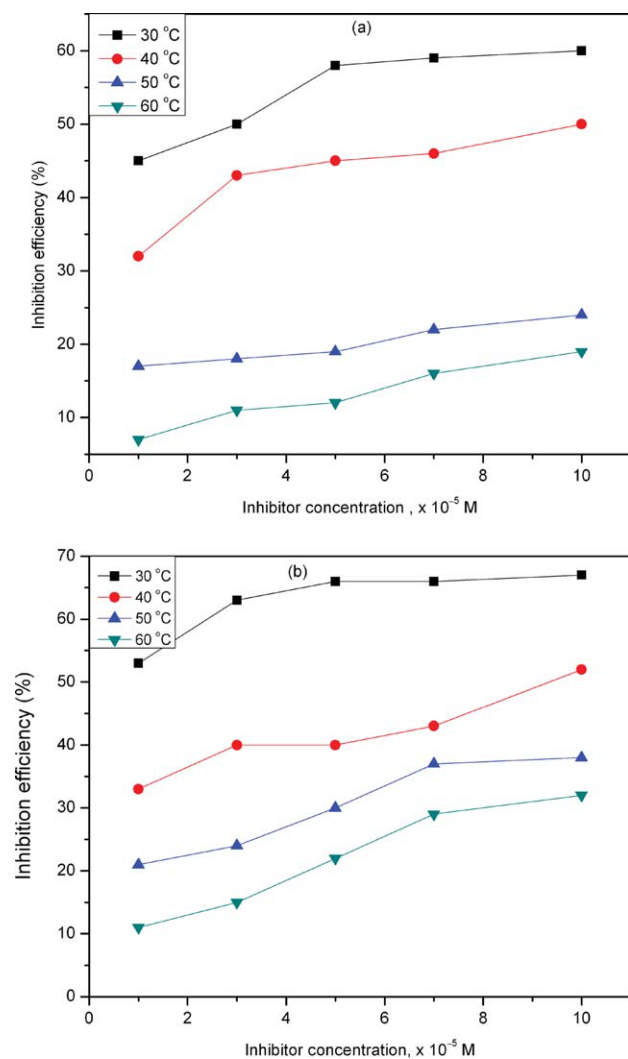


Figure 2 Plot of inhibition efficiency against inhibitor concentration for mild steel corrosion in 0.5 M H₂SO₄ in presence of (a) PEG and (b) PVP at different temperatures from weight loss measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

efficiencies can be found in the literature.^{49–51} It has been reported that the adsorption of organic inhibitors mainly depends on some physicochemical properties of the molecules related to its functional groups, to the possible steric effect and electronic density of donor atoms.⁵² It is generally believed that the adsorption of inhibitor depends on the nature and state of the metal surface, the type of corrosive medium and the chemical structure of the inhibitor.⁵³ Also adsorption takes place through heteroatoms such as nitrogen, oxygen, sulphur, and phosphorous, triple bonds or aromatic rings. The inhibition efficiency should increase⁵⁴ in the order $P > S > N > O$. Examination of the chemical structures of PEG and PVP repeat units (Fig. 1) reveal some differences, while PEG contains only O hetero-

atom, PVP contains N in addition to O atoms. The adsorption of both PEG and PVP through these heteroatoms onto the mild steel surface will create a barrier for charge and mass transfers and thus isolate the metal from further attack from the corrosive agents present in solution hence the observed inhibiting effect. However, the presence of cyclic ring in PVP leads to increase in electron density on nitrogen atom (which is absent in PEG). The increase in electron density causes the molecule of PVP to be stabilized. The stabilization energy results in enhancing the surface coverage of the mild steel surface through the nitrogen atom anchoring around which the electron density is increased.⁵⁵ Therefore the surface coverage in this case is expected to increase and results in increase of inhibition efficiency.

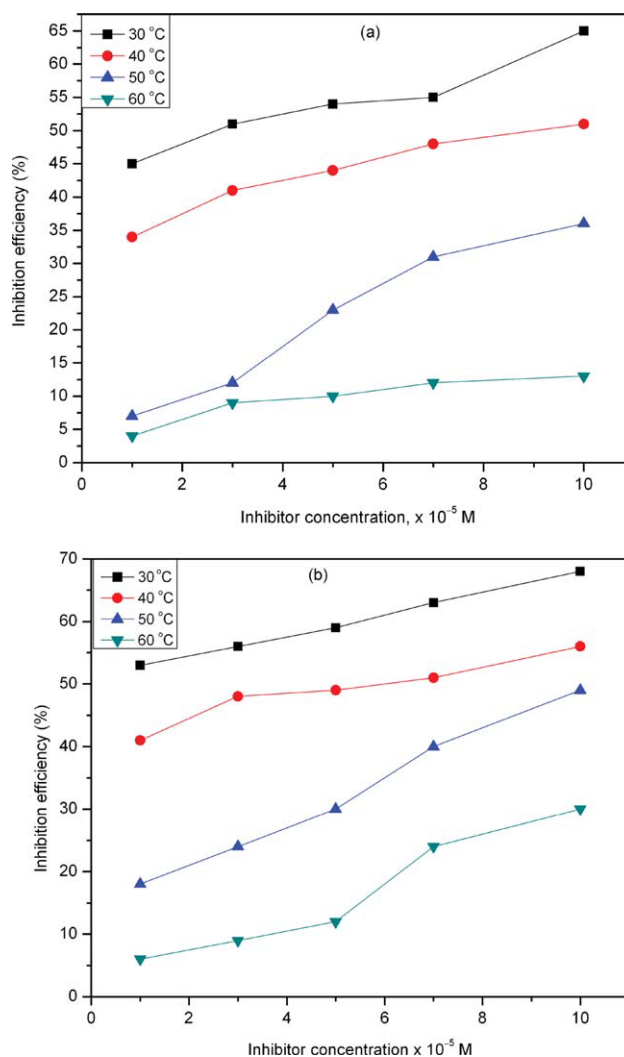


Figure 3 Plot of inhibition efficiency against inhibitor concentration for mild steel corrosion in 1 M H₂SO₄ in presence of (a) PEG and (b) PVP at different temperatures from hydrogen evolution measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

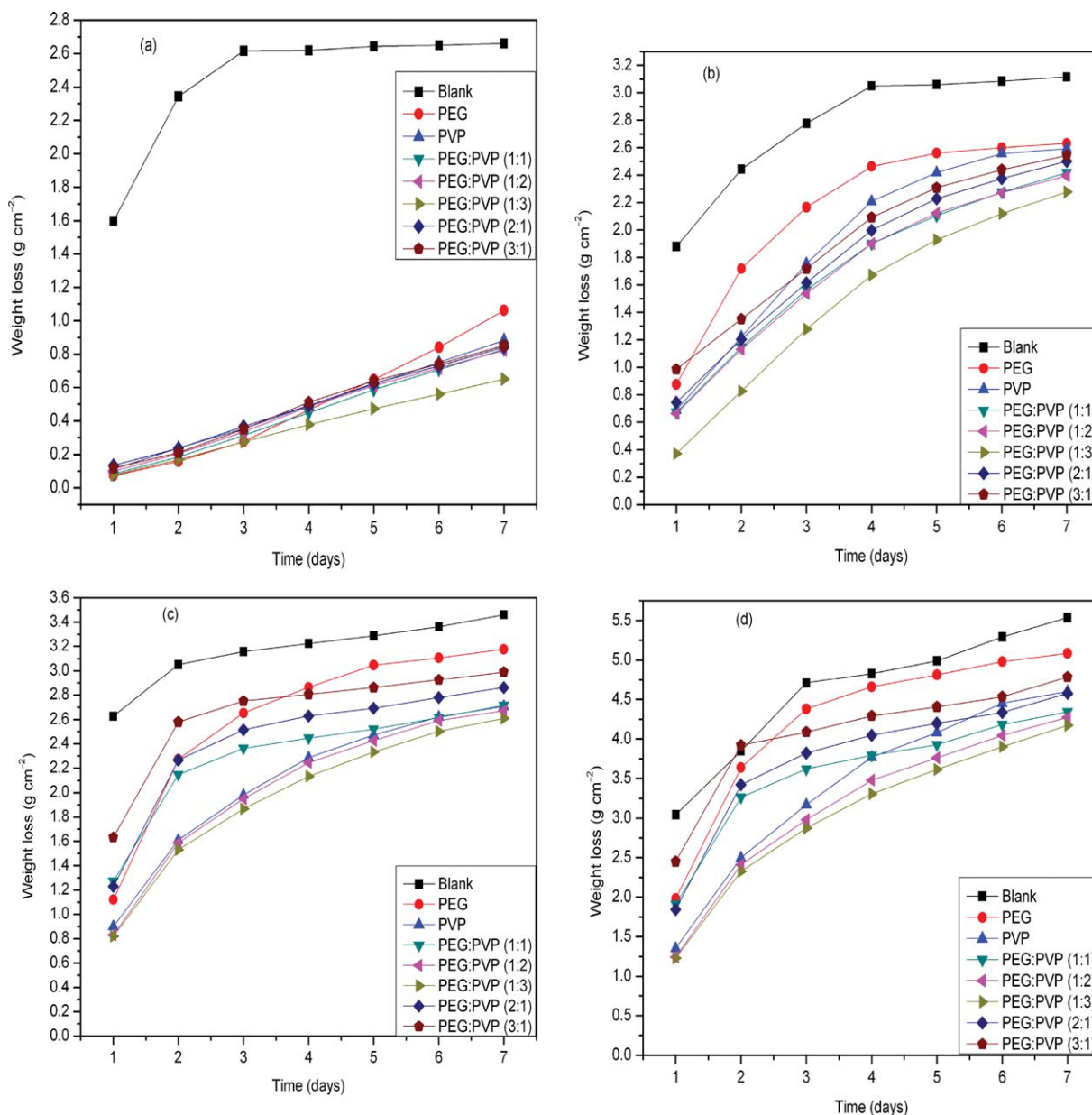


Figure 4 Variation of weight loss against time for mild steel corrosion in 0.5 M H₂SO₄ in the absence and presence of PEG, PVP, and PEG–PVP blends at (a) 30, (b) 40, (c) 50, and (d) 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Inhibition by PEG–PVP blends

Weight loss measurements

The corrosion and corrosion inhibition behavior of metals and alloys in acidic environment can be determined using different electrochemical and non-electrochemical techniques. For the non-electrochemical techniques, weight loss method is ideally suited for long term immersion test. Corroborative results between weight loss and electrochemical impedance spectroscopy,⁵⁶ potentiodynamic polarization⁵⁷ and thermometric⁵⁸ techniques have been reported. Results obtained in the present study show that the highest inhibition efficiency was obtained at $1 \times$

10^{-4} M PEG and PVP concentration from the weight loss measurements. This concentration was therefore chosen to evaluate the effect of PEG–PVP blends on the corrosion inhibition of mild steel in 0.5 M H₂SO₄. Figure 4 shows the plot of weight loss against time for mild steel in 0.5 M H₂SO₄ in the absence and presence of PEG, PVP and the different blending ratios at 30, 40, 50, and 60°C represented by panels a, b, c, and d, respectively. Inspection of the figure reveals that the weight loss of mild steel was reduced in the presence of PEG and PVP compared to the free acid solution. This indicates that both PEG and PVP act as inhibitors for the acid induced corrosion of mild steel. Also the weight loss

TABLE I
Calculated Values of Corrosion Rate for Mild Steel in 0.5 M H₂SO₄ in the Absence and Presence of PEG, PVP, and Their Blends at Different Temperatures

System/concentration	Corrosion rate $\times 10^{-3}$ (mm/yr)			
	30°C	40°C	50°C	60°C
Blank	4.88 \pm 0.021	5.71 \pm 0.021	6.35 \pm 0.016	10.15 \pm 0.031
PEG (1×10^{-4} M)	1.95 \pm 0.012	2.83 \pm 0.011	4.83 \pm 0.016	9.33 \pm 0.022
PVP (1×10^{-4} M)	1.62 \pm 0.021	2.76 \pm 0.017	3.96 \pm 0.021	8.44 \pm 0.017
PEG : PVP (1 : 1)	1.52 \pm 0.010	2.44 \pm 0.012	3.98 \pm 0.016	7.97 \pm 0.021
PEG : PVP (1 : 2)	1.51 \pm 0.013	2.39 \pm 0.010	3.89 \pm 0.012	7.84 \pm 0.016
PEG : PVP (1 : 3)	1.19 \pm 0.021	2.18 \pm 0.010	3.78 \pm 0.012	7.66 \pm 0.021
PEG : PVP (2 : 1)	1.54 \pm 0.014	2.59 \pm 0.012	4.25 \pm 0.021	8.39 \pm 0.012
PEG : PVP (3 : 1)	1.56 \pm 0.012	2.67 \pm 0.016	4.48 \pm 0.021	8.78 \pm 0.010

in the presence of PVP was lower than in the presence of PEG, which suggests that PVP is a better inhibitor than PEG. Further reduction in weight loss was observed on blending the two polymers. Weight loss reduction increases with increasing amount of PVP in the blends and vice versa with the most pronounced effect noticed with PEG : PVP ratio of 1 : 3. Further examination of the plots show that weight loss increases with increase in temperature with greater weight loss obtained at 60°C for all the systems studied. The calculated values of corrosion rate (mm/yr) for mild steel in 0.5 M H₂SO₄ in the absence and presence of different additives are listed in Table I. From the table, it is clearly seen that the corrosion rate of mild steel in 0.5 M H₂SO₄ is lower in the presence of the additives compared to the blank solution. Again corrosion rate is observed to be lower in the presence of blended PEG and PVP compared to individual polymers especially with increasing amount of PVP in the blend. The data in Table I also indicate that the rates of mild steel corrosion in the absence and presence of the PEG, PVP, and their blends increased with rise in temperature in the acidic medium. This could be attributed to the fact that increase in temperature usually accelerates corrosive processes, particularly in media in which hydrogen gas evolution accompanies corrosion, giving rise to higher dissolution rates of the metal. Similar observation has been reported by other authors.^{42,44} Figure 5 shows the plot of inhibition efficiency against PEG : PVP blending ratio at different temperatures. The plot reveals that inhibition efficiency increases with increase in the amount of PVP in the blend and vice versa. Also, inhibition efficiency increases with decrease in temperature with the highest values obtained at 30°C for all the blending ratios studied. The decrease in inhibition efficiency with increase in temperature suggests that the inhibitors were physically adsorbed onto the mild steel surface even in their blended form. Comparing the inhibition efficiency of PEG–PVP blend in Figure 5 and the individual homopolymers in Figure 2, it is observed that the inhibition efficiency

of the blended polymer was higher than that of the individual homopolymers. For instance at 30°C, the inhibition efficiency for PEG and PVP were 60 and 67%, respectively, at the highest concentration (1×10^{-4} M) studied. On blending the polymers, inhibition efficiency increases especially with increasing amount of PVP with the highest inhibition efficiency of 76% obtained at the blending ratio of 1 : 3 (PEG : PVP), This suggests a synergistic inhibition effect between the two polymers.

Hydrogen evolution measurements

The gasometric technique provides a rapid and reliable means for the assessment of inhibitive performance of corrosion inhibitors on mild steel corrosion in acidic media at short term immersion period. The relative speed and effectiveness of the gasometric technique as well as its suitability for *in situ* monitoring, any perturbation by an inhibitor with respect

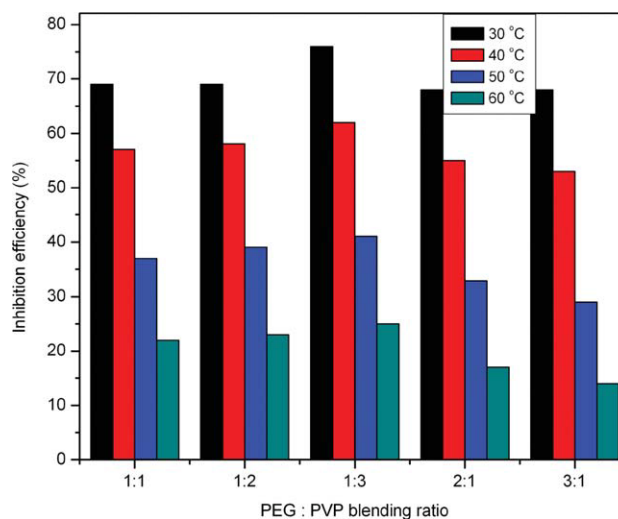


Figure 5 Plot of inhibition efficiency against PEG: PVP blending ratio for mild steel corrosion in 0.5 M H₂SO₄ at different temperatures from weight loss measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

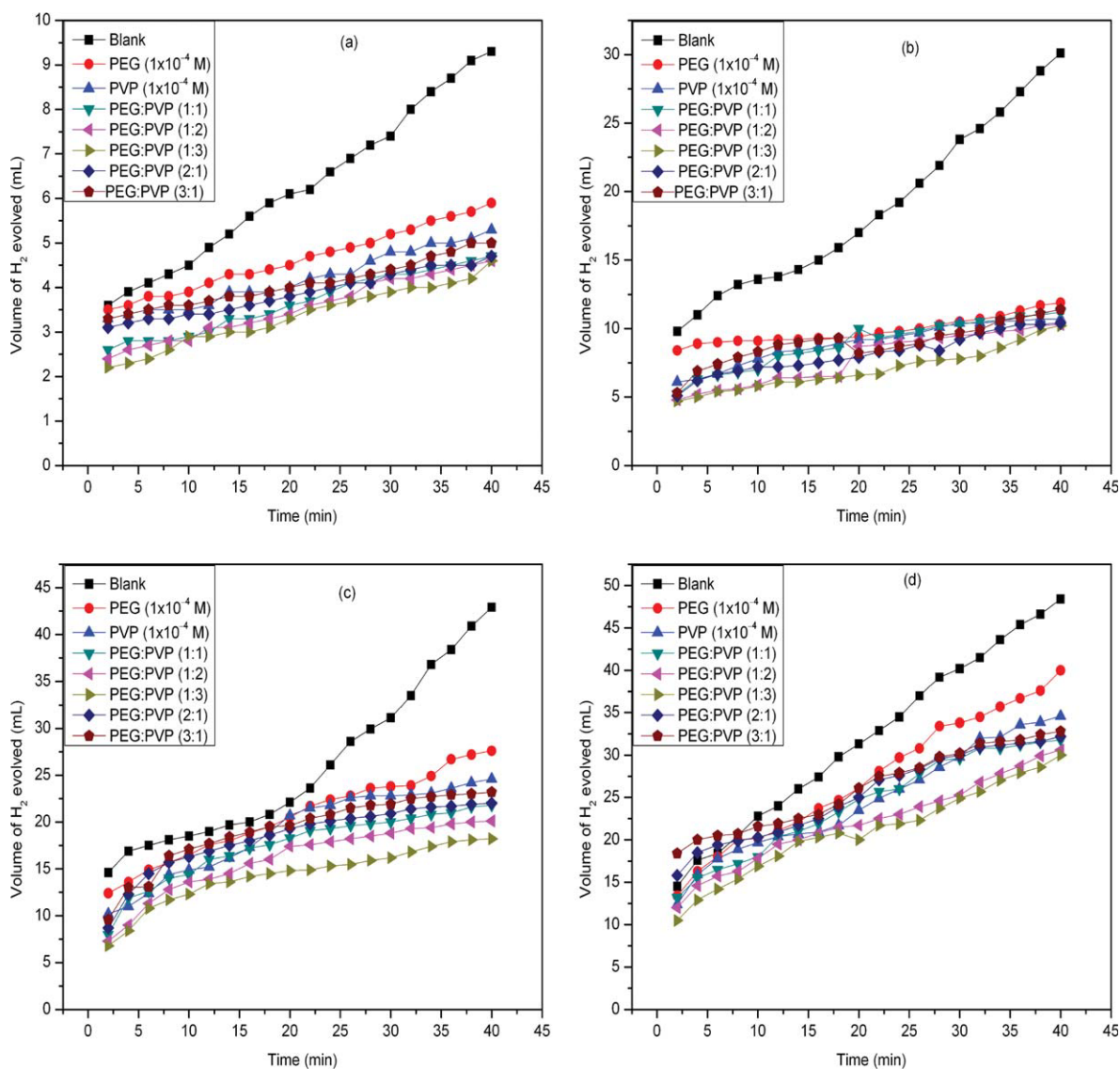


Figure 6 Variation of volume of H_2 evolved with time for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of PEG, PVP, and PEG–PVP blends at (a) 30, (b) 40, (c) 50, and (d) 60°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

to gas evolution in the metal/solution systems have been established in the literature.^{1,59–61} The volume of H_2 gas evolved in both inhibited and uninhibited 1 M H_2SO_4 solutions were monitored as a function of immersion time at fixed time interval. Figure 6 shows the plot of volume of H_2 gas evolved against time for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of PEG, PVP, and their different blending ratios at (a) 30, (b) 40, (c) 50, and (d) 60°C, respectively. Inspection of the figure shows a remarkable increase in the volume of H_2 gas evolved in the free acid solution at all the temperatures studied. This has been attributed to increased surface area of the mild steel as a result of excess iron dissolution.¹ On the introduction of both PEG and PVP into the corrosive medium, it is seen that there is a considerable reduction in the volume of

H_2 gas evolved, suggesting that both PEG and PVP molecules adsorbed onto the metal surface and blocked the electrochemical reaction efficiently by decreasing the available surface area. Further reduction in the volume of H_2 gas evolved was observed on blending the two polymers with the most pronounced effect noticed at PEG : PVP blending ratio of 1 : 3 which is in good agreement with the results of the weight loss measurements. Also the volume of H_2 gas evolved increases with increase in temperature for all the systems studied.

The plot of inhibition efficiency against PEG : PVP blending ratio at different temperatures from the hydrogen evolution measurements is shown in Figure 7. The plot reveals that inhibition efficiency increases with increase in the amount of PVP in the blend and vice versa. Also, inhibition efficiency

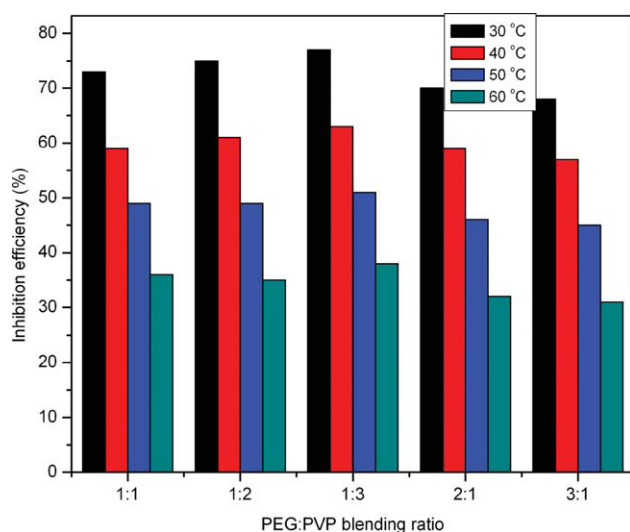


Figure 7 Plot of inhibition efficiency against PEG : PVP blending ratio for mild steel corrosion in 1 M H₂SO₄ at different temperatures from hydrogen evolution measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increases with decrease in temperature with the highest values obtained at 30 °C for all the blending ratios studied. The decrease in inhibition efficiency with increase in temperature suggests that the inhibitors were physically adsorbed onto the mild steel surface. Comparison of the values of inhibition efficiency from the two independent methods as presented in Figure 5 and 6 for weight loss and hydrogen evolution techniques, respectively, it is observed that the values obtained from the hydrogen evolution technique are higher at all PEG : PVP blending ratios and temperatures. This can be attributed to differences in immersion time needed for the inhibiting species to get adsorbed and form a protective film on the mild steel surface thereby isolating the metal from attack of the aggressive anions present in solution. In addition, it has been argued that corrosion rate values from hydrogen evolution method represent instantaneous values while those one from weight loss method represent average values.⁴⁷

Adsorption studies

It is acknowledged that adsorption isotherms provide useful insights into the characteristics of the adsorption process and the mechanism of corrosion inhibition.⁶² To clarify the nature of adsorption, the degree of surface coverage (θ) values for the different concentrations of PEG and PVP at different temperatures were computed from the weight loss measurements as follows: $\eta\% = \theta \times 100$ (assuming a direct relationship between surface coverage and inhibition efficiency) and then fitted theoretically to different adsorption isotherms. Langmuir adsorption

isotherm was first to be tested. This isotherm postulates monolayer adsorption hence no interaction between the adsorbate species on the metal surface and in such circumstances, the slope should be unity. Langmuir isotherm is given by:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (6)$$

The plot of C/θ is shown to be linear in Figure 8 for (a) PEG and (b) PVP, and the adsorption parameters are given in Table II. Though the linearity and good correlation coefficient (R^2) of the Langmuir plot may be taken to suggest that the adsorption of both PEG and PVP follow the Langmuir isotherm, the considerable deviation of the slope from unity indicates the isotherm can not be strictly applied. The deviation of the slope from unity as observed in

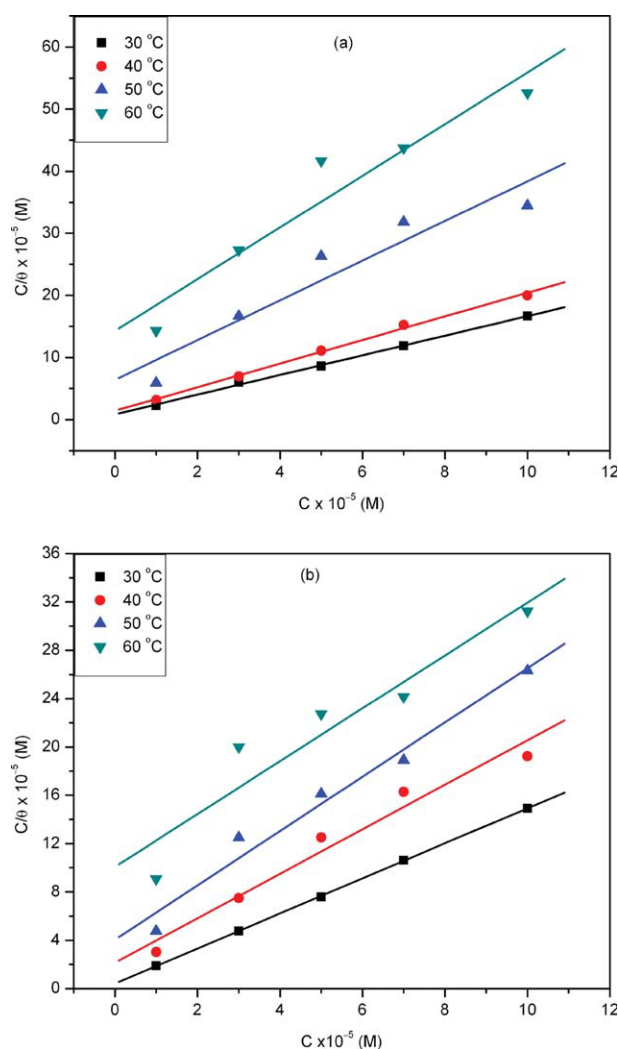


Figure 8 Langmuir adsorption isotherm model for mild steel in 0.5 M H₂SO₄ containing (a) PEG and (b) PVP at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Adsorption Parameters Derived from Langmuir and Temkin Adsorption Isotherms
for PEG and PVP at Different Temperatures

Inhibitor	Temperature (°C)	Langmuir				Temkin			
		$\Delta G_{\text{ads}}^{\circ}$ (kJ/mol)	K_{ads}	Slope	R^2	$\Delta G_{\text{ads}}^{\circ}$ (kJ/mol)	K_{ads}	a (M^{-1})	R^2
PEG	30	-10.52	1.17	1.58	0.99	-17.43	18.19	-0.082	0.97
	40	-9.56	0.71	1.89	0.99	-17.53	13.14	-0.085	0.98
	50	-5.87	0.16	3.19	0.95	-14.78	4.42	-0.049	0.80
	60	-3.76	0.07	4.16	0.96	-15.13	4.25	-0.056	0.95
PVP	30	-12.33	2.46	1.45	0.99	-17.41	18.03	-0.071	0.96
	40	-8.49	0.47	1.84	0.98	-17.16	13.14	-0.079	0.91
	50	-7.06	0.25	2.25	0.99	-17.65	12.89	-0.092	0.94
	60	-4.45	0.09	2.19	0.95	-18.60	14.91	-0.108	0.95

this study could be interpreted to mean that there are interactions between adsorbate species on the metal surface.

The Temkin and Frumkin isotherms are commonly used to quantify the interactions occurring between adsorbate species on a metal surface. The values of R^2 indicate that Temkin isotherm was most applicable in this present study. The characteristics of Temkin adsorption isotherm is given by the equation:

$$\exp(-2a\theta) = K_{\text{ads}}C \quad (7)$$

where ' a ' is molecules interaction parameters, θ is the degree of surface coverage, ' C ' is the concentration of the inhibitor, and K_{ads} is the equilibrium constant of adsorption process. The equilibrium constant of adsorption process (K_{ads}) is related to the free energy of adsorption, $\Delta G_{\text{ads}}^{\circ}$ by the equation:

$$K_{\text{ads}} = \frac{1}{55.5} \exp \left[\frac{-\Delta G_{\text{ads}}^{\circ}}{RT} \right] \quad (8)$$

where 55.5 is the moles of water in mol dm^{-3} . Figure 9 shows the plot of θ against $\log C$ for (a) PEG and (b) PVP at different temperatures (30–60°C). Linear plots were obtained which shows that the adsorption of both PEG and PVP onto mild steel surface follow Temkin adsorption isotherm. Adsorption parameters derived from the plots are listed in Table II. The equilibrium constant whose values indicate the binding power of the inhibitor to the metal surface is seen to decrease with increasing temperature. Such behaviour can be interpreted on the basis that an increase in temperature results in the desorption of some adsorbed molecules on the metal surface and is consistent with the proposed physisorption mechanism.⁶³ Also, large values of K_{ads} imply more efficient adsorption hence better inhibition efficiency.⁶⁴ The large values of K_{ads} obtained for both PEG and PVP at 30°C accord with the high inhibition efficiency obtained at this tem-

perature. In all cases, the values of molecular interaction parameter ' a ' are negative, indicating that repulsion exists in the adsorption layer.⁶⁵

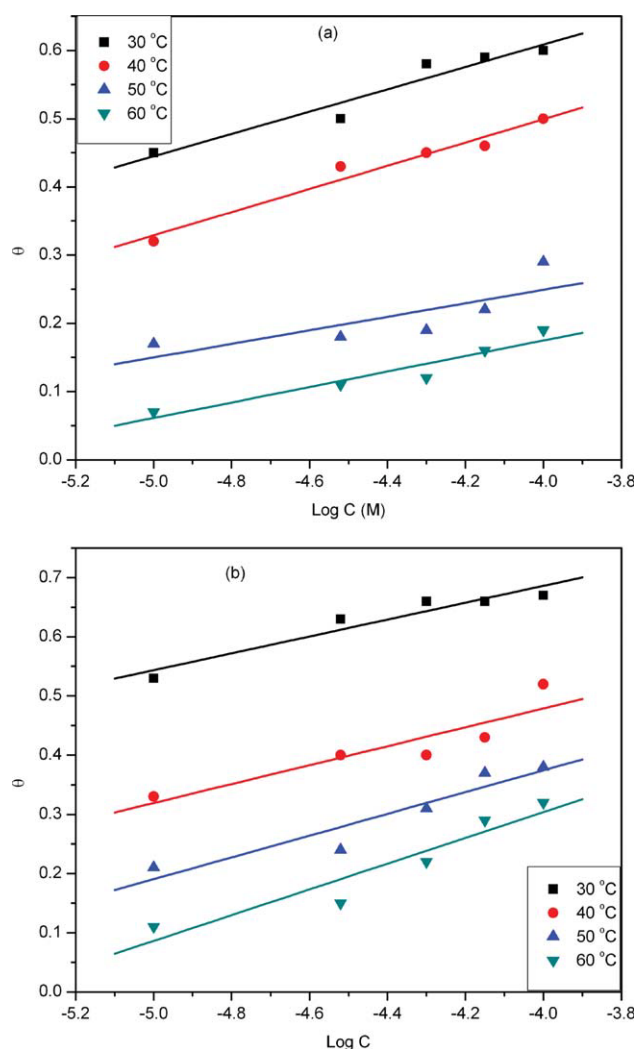


Figure 9 Temkin adsorption isotherm model for mild steel in 0.5 M H_2SO_4 containing (a) PEG and (b) PVP at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

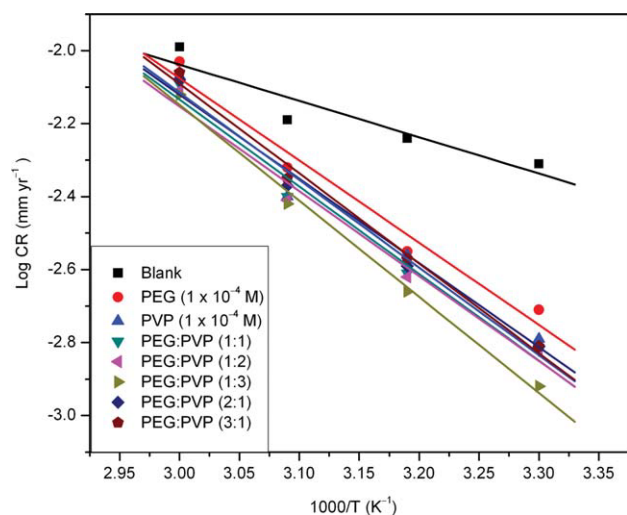


Figure 10 Arrhenius plot for mild steel corrosion in 0.5 M H₂SO₄ in the absence and presence of PEG, PVP, and PEG–PVP blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The free energy of adsorption $\Delta G_{\text{ads}}^{\circ}$ was calculated using eq. (8), and the values are listed in Table II for PEG and PVP at the different temperatures studied. The negative values of $\Delta G_{\text{ads}}^{\circ}$ reveal that the adsorption process takes place spontaneously. It is well known that the absolute values of $\Delta G_{\text{ads}}^{\circ}$ of the order 20 kJ mol⁻¹ or lower indicate physisorption while those of the order 40 kJ mol⁻¹ or higher indicate chemisorption.⁶⁶ Accordingly, the values of $\Delta G_{\text{ads}}^{\circ}$ obtained in the present study are below 20 kJ mol⁻¹ and is therefore consistent with physisorption mechanism.

Effect of temperature

The effect of temperature on the inhibited acid–metal reaction is highly complex, because many changes occur on the metal surface such as rapid etching, desorption of the inhibitor, and the inhibitor may undergo decomposition and/or rearrangement.

To evaluate the effect of temperature on the adsorption behavior as well as the activation parameters of the corrosion processes of mild steel in 0.5 M H₂SO₄ in the blank solution and solutions containing PEG, PVP, and the different blending ratios, the weight loss measurements were carried out in the temperature range of 30–60°C. The influence of temperature on the corrosion rates and inhibition efficiency for the different systems are illustrated in Table I, Figures 2 and 5. As it is seen, the corrosion rate for mild steel increases to a large extent with temperature in uninhibited solution than in inhibited solution. This result confirms that PEG, PVP, and their blends decrease the corrosion process acting as an efficient corrosion inhibitor. Lowering corrosion action is enhanced more at lower temperatures compared to the higher ones as seen in Table I.

The apparent activation energy, E_a , of the corrosion reaction was determined using Arrhenius plots. Arrhenius equation is given by the expression:

$$\log \text{CR} = \log A - \left(\frac{E_a}{2.303RT} \right) \quad (9)$$

where CR is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature, and A is the frequency factor. Figure 10 shows Arrhenius plots of logarithm of corrosion rate ($\log \text{CR}$) versus $1/T$ for mild steel in the corrosive medium with and without addition of PEG, PVP, and their blends in different ratios. Straight lines were obtained with a slope of $(-E_a/2.303R)$ from which E_a values were computed and listed in Table III. From the table, it can be seen that E_a is higher in the presence of the additives than in the blank acid. This observation further supports the proposed physisorption mechanism because unchanged or lower E_a in inhibited systems compared to blank has been reported⁶⁰ to be indicative of chemical adsorption mechanism whereas increased E_a suggests a physical adsorption mechanism. The enthalpy of activation (ΔH^*) and the

TABLE III
Kinetic and Thermodynamic Parameters for Mild Steel Corrosion in 0.5 M H₂SO₄ Without and With PEG, PVP, and Their Blends

System/concentration	E_a (kJ/mol)	Q_{ads} (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)
Blank	19.05 ^a (0.94)	–	15.78 ^a (0.94)	–237.73 ^a (0.94)
PEG (1 × 10 ⁻⁴ M)	43.13 (0.98)	–79.91 (0.97)	40.45 (0.98)	–164.22 (0.98)
PVP (1 × 10 ⁻⁴ M)	44.14 (0.98)	–61.53 (0.98)	41.47 (0.98)	–162.04 (0.98)
PEG : PVP (1 : 1)	45.67 (0.99)	–58.11 (0.99)	42.02 (0.99)	–160.82 (0.99)
PEG : PVP (1 : 2)	44.52 (0.99)	–55.95 (0.99)	42.02 (0.99)	–161.01 (0.99)
PEG : PVP (1 : 3)	50.37 (0.99)	–63.19 (0.99)	48.46 (0.99)	–141.57 (0.99)
PEG : PVP (2 : 1)	45.92 (0.99)	–65.85 (0.99)	43.79 (0.99)	–154.80 (0.99)
PEG : PVP (3 : 1)	47.10 (0.99)	–72.38 (0.99)	42.82 (0.99)	–157.53 (0.99)

^a Values in parentheses represent R^2 values.

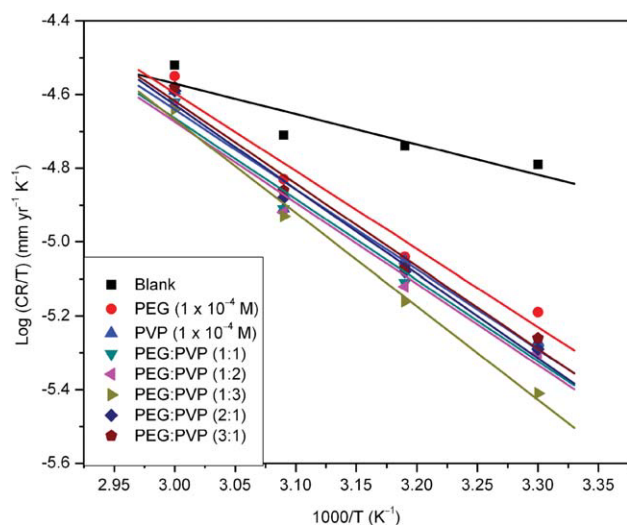


Figure 11 Transition state plot for mild steel corrosion in 0.5 M H₂SO₄ in the absence and presence of PEG, PVP, and PEG–PVP blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

entropy of activation (ΔS^*) for the corrosion of mild steel in 0.5 M H₂SO₄ was obtained by applying transition state equation⁶⁷:

$$\log\left(\frac{CR}{T}\right) = \left[\log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S^*}{2.303R}\right)\right] - \frac{\Delta H^*}{2.303RT} \quad (10)$$

where CR is the corrosion rate, h is the Planck's constant, N is the Avogadro's number, R is the universal gas constant, and T is the absolute temperature. A plot of $\log (CR/T)$ versus $1/T$ as depicted in Figure 11 gave straight lines from which the values of ΔH^* and ΔS^* were computed from the slope ($-\Delta H^*/2.303R$) and intercept [$\log (R/Nh) + (\Delta S^*/2.303R)$], respectively, and listed in Table III. The data in the table show that ΔH^* vary in the same manner with E_a values being higher in the presence of the additives compared to the free acid solution. The adsorption of the inhibitors is assumed to occur on the higher energy sites and the presence of inhibitor, which results in the blocking of the active sites, must be associated with an increase in the activation energy of mild steel corrosion in the inhibited state.⁶⁸ The highest values of the thermodynamic functions (E_a and ΔH^*) obtained for PEG : PVP blend ratio of 1 : 3 indicates that more energy barrier for the reaction is attained which accord with the highest inhibition efficiency at this blending ratio of PEG and PVP. The entropy of activation, ΔS^* in the absence and presence of the additives is large and negative. This has been widely reported^{68–72} to indicate that the activated complex in the rate determining step represents an association rather than a

dissociation step, meaning that, a decrease in disordering takes place on going from reactants to the activated complex. Further insight into the adsorption mechanism is offered by considering the thermodynamic functions for the mild steel dissolution in 0.5 M H₂SO₄ in the presence of PEG, PVP, and the PEG–PVP blend in different ratios. In this regards, heat of adsorption (Q_{ads}) was evaluated from the variation of surface coverage with reciprocal of temperature from the kinetic thermodynamic model^{61,73}:

$$\log\left(\frac{\theta}{1-\theta}\right) = \log A + \log C - \frac{Q_{ads}}{2.303RT} \quad (11)$$

where A is a constant, C is the inhibitor concentration, θ is the occupied, and $(1 - \theta)$ is the vacant site not occupied by the inhibitor. The plot of $\log [\theta/(1 - \theta)]$ as a function of $1/T$ for the different additives is shown in Figure 12. The values of heat of adsorption were estimated from the slope of the linear plots and are listed in Table III. In all cases, the values of Q_{ads} are negative indicating that the inhibitor adsorption and hence inhibition efficiency decreases with rise in temperature. The negative values of heat of adsorption obtained also support the physical adsorption mechanism proposed.

Synergism considerations

The existence of synergism phenomenon between PEG and PVP was evaluated by estimating the synergism parameter, S_1 from the inhibition efficiency values from the two techniques employed using the expression,^{20,74}

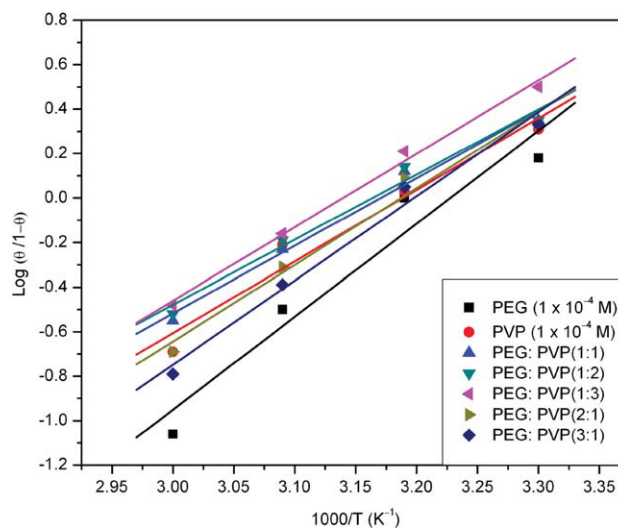


Figure 12 Plot of $\log (\theta/(1 - \theta))$ against $1/T$ at for PEG, PVP, and PEG–PVP blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
Synergism Parameter (S_1) for Different PEG : PVP
Blending Ratios at 30°C from Weight Loss and
Hydrogen Evolution Measurements

Polymer blending ratio	Synergism parameter (S_1)	
	Weight loss method	Hydrogen evolution method
PEG : PVP (1 : 1)	1.85	1.86
PEG : PVP (1 : 2)	1.85	1.86
PEG : PVP (1 : 3)	1.88	1.86
PEG : PVP (2 : 1)	1.88	1.86
PEG : PVP (3 : 1)	1.88	1.92

$$S_1 = \frac{1 - \eta_1 - \eta_2 + \eta_1 \eta_2}{1 - \eta_{12}} \quad (12)$$

where η_1 is inhibition efficiency of the PEG, η_2 is the inhibition efficiency of PVP, and η_{12} is measured inhibition efficiency for the PEG in combination with PVP. The calculated values of the synergism parameter for the different PEG–PVP blending ratios are listed in Table IV. The values of the synergism parameter as observed in the table are greater than unity which indicates that the enhanced inhibition efficiency exhibited by PEG–PVP combination is synergistic in nature. Synergistic effect between mixture formulations (usually between anions or cations and neutral molecules) is usually attributed to co-adsorption of the two compounds which may be either competitive or co-operative.^{8,12} In competitive adsorption, the anion and cation are adsorbed at different sites on the metal surface. The adsorption of an anion may enhance the adsorption of a cation and vice versa. In co-operative adsorption, the anion is chemisorbed on the surface, and the cation is adsorbed on a layer of the anion. Both co-operative and competitive adsorption mechanism may occur simultaneously.¹² Specifically, synergistic effect between halide ions and organic compounds in acidic medium have been attributed to the initial specific adsorption of the halide ions which then improves adsorption of the organic cations by forming intermediate bridges between the positively charged metal surface and the positive end of the organic inhibitor. Corrosion inhibition synergism thus results from increased surface coverage arising from ion-pair interactions between the organic cations and the anions. The mechanism of synergistic effect between PEG and PVP observed in this present study is not entirely clear. Although, the possibility of chemisorption of one the inhibitors is capable of decreasing the hydrophilicity of metal surfaces, which is likely to promote adsorption of organic molecules as suggested by Kuznetsov and Andreev⁷⁵ may not be ruled out. However, a more

specific experiment will be required to clarify this phenomenon which is currently being pursued in our laboratory.

CONCLUSIONS

The corrosion and corrosion inhibition behavior of PEG, PVP, and PEG–PVP blends for mild steel in H_2SO_4 solution was investigated. From the experimental results obtained, the following conclusions can be drawn:

1. PEG and PVP act as inhibitors for acid induced corrosion of mild steel, and the extent of inhibition was found to be concentration dependent. Inhibition efficiency increases with increase in concentration but decreases with rise in temperature. PVP proved to be a better inhibitor than PEG.
2. On blending both polymers, inhibition efficiency was found to be enhanced which can be ascribed to synergistic effect. The optimum blending ratio (PEG : PVP) of 1 : 3 gave the maximum inhibition efficiency for mild steel in the acid medium.
3. The adsorption characteristics of both PEG and PVP can be approximated by Temkin adsorption isotherm.
4. Physical adsorption mechanism is proposed from the trend of inhibition efficiency with temperature, which is also corroborated by kinetic and thermodynamic parameters obtained.

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