

The inhibition action of *N*-furfuryl-*N'*-phenyl thiourea on the corrosion of mild steel in acid media

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Abstract: The inhibiting effect of *N*-furfuryl-*N'*-phenyl thiourea (FPTU) on the corrosion of mild steel in aqueous solutions of 0.05 and 0.1 M HCl, as well as 0.025 and 0.05 M H₂SO₄ has been demonstrated using the potentiodynamic polarization technique. The polarization data showed that FPTU acts as an efficient anodic inhibitor for mild steel in both acid solutions. A very high inhibition efficiency was evidenced in both acid solutions and it was found to vary with the concentration of the inhibitor and temperature. The obtained kinetic parameters of adsorption revealed spontaneous adsorption and a strong interaction of FPTU with the mild steel surface.

Keywords: *N*-furfuryl-*N'*-phenyl thiourea, mild steel, corrosion, corrosion inhibitor, hydrochloric acid, sulphuric acid.

INTRODUCTION

Mild steel is one of the major construction material, which is extensively used in chemical and allied industries for the handling of acid, alkali and salt solutions.¹ The study of the corrosion of mild steel in acid media, which is of both academic and industrial concern, has received a considerable amount of attention.² Acid solutions are widely used in industry, the most important fields of application being acid pickling, industrial acidcleaning, acid descaling and oil and gas well acidizing.^{3,4} The use of inhibitors is one of the most practical methods for protection against metallic corrosion, especially in acid media.⁵ However, the methods of corrosion inhibition must be evaluated according to the parameters of the particular corrosion system, as preventive measures designed for application in one environment may fail for the same metal under different conditions. There is a continuous search for better inhibitors to meet the needs of industry because of the vast differences in the media encountered in industry. The effect of temperature on the inhibition process is of great industrial importance.

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Effective inhibitors are expected to perform under a wide range of conditions. Corrosion is more severe during the pickling and cleaning of metals and alloys at elevated temperatures using acid solutions; hence, special attention must be paid to the selection of inhibitors for such practical applications.⁶

The selection of appropriate inhibitors mainly depends on the type of acid, its concentration, temperature and velocity of flow, the presence of dissolved inorganic and/or organic substances, even in minor amounts and, of course, on the type of metallic material exposed to the action of the acidic solutions. Considering the technical process of pickling, good inhibitors must meet quite a number of requirements, such as effective inhibition of metal dissolution, no over-pickling in the presence of higher valency cations, no delay of the pickling process, effective at low concentrations and higher temperatures, thermally and chemically stable, effective inhibition of hydrogen up-take by the metal, good surfactant characteristics and good foaming characteristics.³

Most of the efficient inhibitors used in industry are organic compounds having multiple bonds in their molecules, which mainly contain nitrogen and sulphur atoms through which they are adsorbed on the metal surface. Among these thiourea and its derivatives have been extensively used as corrosion inhibitors for various steels in acid media.⁷⁻¹⁵ They are polar molecules with the sulphur atom having a permanent negative charge whereas the nitrogen atom has a positive charge. As the molecule approaches the electrode surface, the electric field of the double layer increases the polarization of molecules and induces additional charges on both sulphur and nitrogen atoms, a condition which enhances the adsorption of molecules.¹⁶ The adsorption depends mainly on the electronic structure of the molecule.¹⁷

Some of the earlier investigated derivatives of thiourea are *N*-methyl thiourea, dimethyl thiourea, tetramethyl thiourea, *N*, *N'*-diethyl thiourea, di-isopropyl thiourea, allyl thiourea, tolyl thiourea, di-orthotolyl thiourea, di-ortoxenyl thiourea, phenyl thiourea, diphenyl thiourea, phenyl *o*-tolyl thiourea, *n*-butyl thiourea, di-*n*-butyl thiourea, and syndiotolyl thiourea.

Already, substituted thioureas have been shown to be fairly effective in corrosion control. The choice of *N*-furfuryl-*N'*-phenyl thiourea (FPTU) is based on the fact that the substituents on the thiourea further increase its electron densities for its adsorption on the metal surface; moreover it can be synthesized conveniently from relatively cheap raw materials. In the present work, the action of FPTU on the corrosion kinetics of mild steel in both hydrochloric and sulphuric acid solutions at four different temperatures and at four levels of inhibitor concentration were investigated using the potentiodynamic polarization technique.

EXPERIMENTAL

Specimens

Mild steel specimens having the composition, (wt %): 0.205 C, 0.06 Si, 0.55 Mn, 0.047 S, 0.039 P with the balance Fe were used for the electrochemical studies. The specimens were mechan-

ically polished with emery papers of 1/0–5/0 grade, thoroughly cleaned with soapy water, rinsed with distilled water and then with alcohol and finally dried in air. The specimen was tightly fitted to one end of a Teflon holder, which exposed a polished surface area of 0.786 cm².

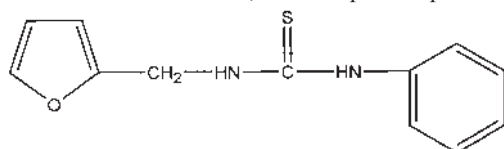


Fig. 1. Structural formula of *N*-furfuryl-*N'*-phenyl thiourea.

Inhibitor

N-furfuryl-*N'*-phenyl thiourea was synthesized by following the reported procedure.¹⁸ The structural formula of FPTU is shown in Fig. 1. The compound was characterized through its spectral data, elemental analysis and melting point (135±1 °C). The results of the elemental analysis were as follows: Calculated for C₁₂H₁₂ON₂S: C 62.04, H 5.21, O 6.89, N 12.06, S 13.80 %. Found: C 61.88, H 5.19, O 6.92, N 12.02, S 13.76 %. The concentration range of the employed inhibitor was 1×10⁻⁴ to 4×10⁻⁴ mol/L for both acid solutions.

Electrolyte

AR grade HCl, H₂SO₄ and distilled water were used to prepare 0.025–0.1 M solutions.

Methodology

The electrochemical studies were performed at room temperature (28 ± 1 °C) using a Wenking potentiostat (LB 95L) and a three electrode cell containing 400 mL of electrolyte, either with or without inhibitor. A platinum foil was used as the auxiliary electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The latter was connected through a Luggin capillary to the cell. The steady state open circuit potential (OCP) was noted at the end of 25–30 min. The potentiodynamic studies were then made from –250 mV *versus* OCP to +250 mV *versus* OCP at a scan rate of 20 mV/min from the cathodic side and the corrosion currents were registered. The experiments were repeated for 40, 45 and 50 °C. From the Tafel plots of potential *versus* log *I*, the corrosion current density (*j*_{corr}) and corrosion potential (*E*_{corr}) were determined. The corrosion rate (*r*), the degree of surface coverage (*θ*) and the percentage inhibition efficiency (% *IE*) were calculated. The results were also confirmed using the linear polarization technique.

RESULTS AND DISCUSSION

The inhibition efficiency and the corrosion rate, determined by the potentiodynamic polarization technique, under the given experimental conditions are presented in Tables I and II. The corrosion rate (*r*), the degree of surface coverage (*θ*) and the percentage inhibition efficiency (% *IE*) of mild steel were calculated using the following relations:

$$r \text{ (mpy)} = \frac{0.1288 \times j_{\text{corr}} \times eq.wt}{D} \quad (1)$$

where *j*_{corr} is the current density in μA/cm², *D* is the specimen density in g/cm³, *eq. wt* is the specimen equivalent weight in grams;

$$\theta = \frac{j_{\text{corr}} - j_{\text{corr}}(\text{inh})}{j_{\text{corr}}} \quad (2)$$

$$\% IE = \frac{j_{\text{corr}} - j_{\text{corr}}(\text{inh})}{j_{\text{corr}}} \cdot 100 \quad (3)$$

where j_{corr} and $j_{\text{corr}}(\text{inh})$ are the current densities in the absence and presence of inhibitor, respectively.

TABLE I. Electrochemical polarization parameters for the inhibition of corrosion of mild steel by FPTU in 0.05 M HCl and 0.025 M H₂SO₄ at different temperatures

| $t/^{\circ}\text{C}$ | $c(\text{FPTU}) \times 10^4$ mol/L | 0.05 M HCl | | | 0.025 M H ₂ SO ₄ | | |
|----------------------|---------------------------------------|-----------------------------|----------------|---------|--|----------------|---------|
| | | $E_{\text{corr}}/\text{mV}$ | r/mpy | $IE/\%$ | $E_{\text{corr}}/\text{mV}$ | r/mpy | $IE/\%$ |
| 28 | 0 | -564 | 192.12 | - | -562 | 25.32 | - |
| | 1 | -519 | 5.09 | 97.35 | -525 | 4.95 | 80.47 |
| | 2 | -501 | 4.30 | 97.76 | -501 | 4.48 | 82.31 |
| | 3 | -495 | 3.83 | 98.01 | -493 | 4.21 | 83.39 |
| | 4 | -488 | 4.23 | 97.80 | -494 | 4.31 | 83.00 |
| 40 | 0 | -562 | 363.87 | - | -560 | 44.83 | - |
| | 1 | -515 | 11.68 | 96.79 | -516 | 7.93 | 82.30 |
| | 2 | -501 | 10.37 | 97.15 | -504 | 7.35 | 83.60 |
| | 3 | -492 | 9.24 | 97.46 | -493 | 6.95 | 84.49 |
| | 4 | -486 | 9.46 | 97.40 | -487 | 7.08 | 84.20 |
| 45 | 0 | -550 | 389.49 | - | -562 | 67.53 | - |
| | 1 | -518 | 13.68 | 96.49 | -524 | 10.67 | 84.20 |
| | 2 | -505 | 12.23 | 96.86 | -508 | 9.72 | 85.60 |
| | 3 | -497 | 11.29 | 97.10 | -486 | 9.18 | 86.41 |
| | 4 | -491 | 11.45 | 97.06 | -495 | 9.32 | 86.20 |
| 50 | 0 | -550 | 422.09 | - | -561 | 95.30 | - |
| | 1 | -518 | 16.16 | 96.17 | -526 | 13.10 | 86.25 |
| | 2 | -508 | 14.44 | 96.58 | -509 | 11.82 | 87.60 |
| | 3 | -499 | 13.51 | 96.80 | -491 | 10.86 | 88.61 |
| | 4 | -495 | 12.87 | 96.95 | -481 | 10.60 | 88.88 |

TABLE II. Electrochemical parameters for the inhibition of corrosion of mild steel by FPTU in 0.1 M HCl and 0.05 M H₂SO₄ at different temperatures

| $t/^{\circ}\text{C}$ | $c(\text{FPTU}) \times 10^4$ mol/L | 0.1 M HCl | | | 0.05 M H ₂ SO ₄ | | |
|----------------------|---------------------------------------|-----------------------------|----------------|---------|---------------------------------------|----------------|---------|
| | | $E_{\text{corr}}/\text{mV}$ | r/mpy | $IE/\%$ | $E_{\text{corr}}/\text{mV}$ | r/mpy | $IE/\%$ |
| 28 | 0 | -540 | 291.09 | - | -557 | 61.13 | - |
| | 1 | -518 | 7.34 | 97.50 | -515 | 6.43 | 89.48 |
| | 2 | -506 | 6.23 | 97.86 | -500 | 5.68 | 90.71 |
| | 3 | -491 | 5.30 | 98.18 | -488 | 5.00 | 91.82 |
| | 4 | -495 | 5.50 | 98.11 | -476 | 5.26 | 91.40 |
| 40 | 0 | -538 | 427.91 | - | -554 | 86.17 | - |
| | 1 | -521 | 13.68 | 96.80 | -524 | 8.80 | 89.79 |
| | 2 | -505 | 12.08 | 97.18 | -514 | 7.71 | 91.05 |
| | 3 | -491 | 10.65 | 97.51 | -506 | 6.76 | 92.15 |

TABLE II. Continued

| $t/^{\circ}\text{C}$ | $c(\text{FPTU}) \times 10^4$ mol/L | 0.1 M HCl | | | 0.05 M H ₂ SO ₄ | | |
|----------------------|---------------------------------------|-----------------------------|----------------|---------|---------------------------------------|----------------|---------|
| | | $E_{\text{corr}}/\text{mV}$ | r/mpy | $IE/\%$ | $E_{\text{corr}}/\text{mV}$ | r/mpy | $IE/\%$ |
| 45 | 4 | -482 | 10.91 | 97.45 | -499 | 7.15 | 91.70 |
| | 0 | -539 | 512.32 | – | -551 | 119.35 | – |
| | 1 | -516 | 17.68 | 96.55 | -529 | 11.82 | 90.10 |
| | 2 | -502 | 15.83 | 96.91 | -514 | 10.32 | 91.35 |
| | 3 | -492 | 14.30 | 97.21 | -502 | 9.08 | 92.39 |
| | 4 | -483 | 14.19 | 97.23 | -504 | 9.55 | 92.00 |
| 50 | 0 | -535 | 547.26 | – | -549 | 157.19 | – |
| | 1 | -519 | 20.30 | 96.29 | -531 | 15.09 | 90.40 |
| | 2 | -508 | 18.33 | 96.65 | -517 | 13.17 | 91.62 |
| | 3 | -496 | 16.96 | 96.90 | -507 | 11.48 | 92.70 |
| | 4 | -486 | 16.58 | 96.97 | -503 | 12.07 | 92.32 |

The effectiveness of FPTU on the corrosion of mild steel was observed by a drastic reduction in the corrosion current density and a positive shift of the corrosion potential (Figs. 2 and 3). The shift in the corrosion potential towards the anodic side indicates that FPTU is an efficient anodic inhibitor for mild steel in both solutions of acids. The inhibition was estimated to be superior by 96 % in HCl and 80 % in H₂SO₄, even at a concentration as low as 1×10^{-4} mol/L. The variation of the inhibition efficiency with increasing concentration of inhibitor is shown in Figs. 4 and 5.

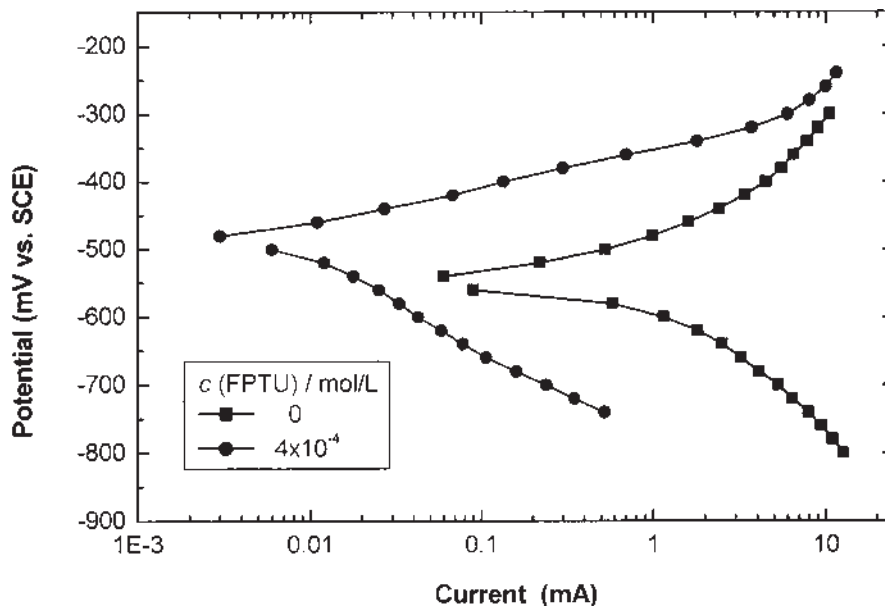


Fig. 2. Potentiodynamic polarization curves for mild steel in 0.1 M HCl without and with FPTU at 28 °C.

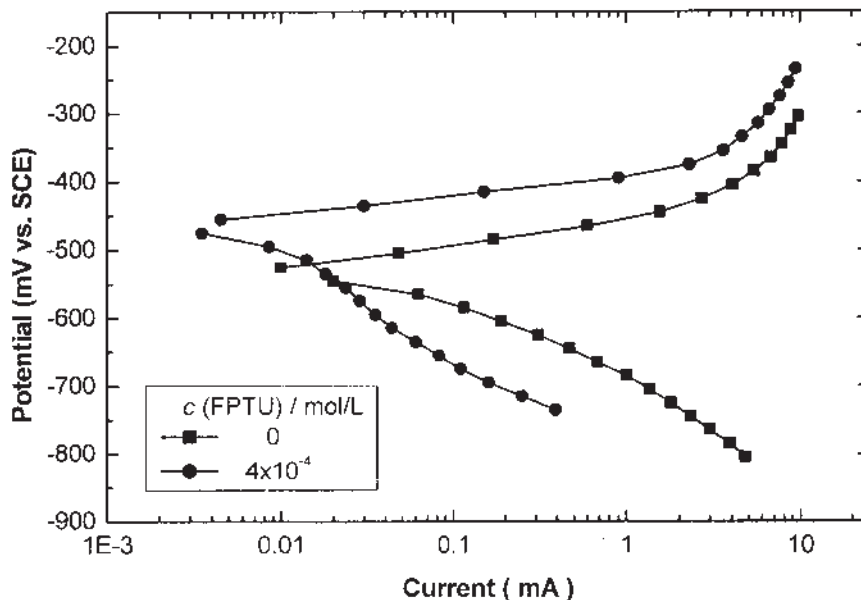


Fig. 3. Potentiodynamic polarization curves for mild steel in 0.05 M H_2SO_4 without and with FPTU at 28 °C.

The *IE* of the compound was found to increase with increasing inhibition concentration at all temperatures up to a critical concentration. The increase in efficiency may be due to the blocking effect of the surface by both the adsorption and film formation mechanism, which decreases the effective area of attack.

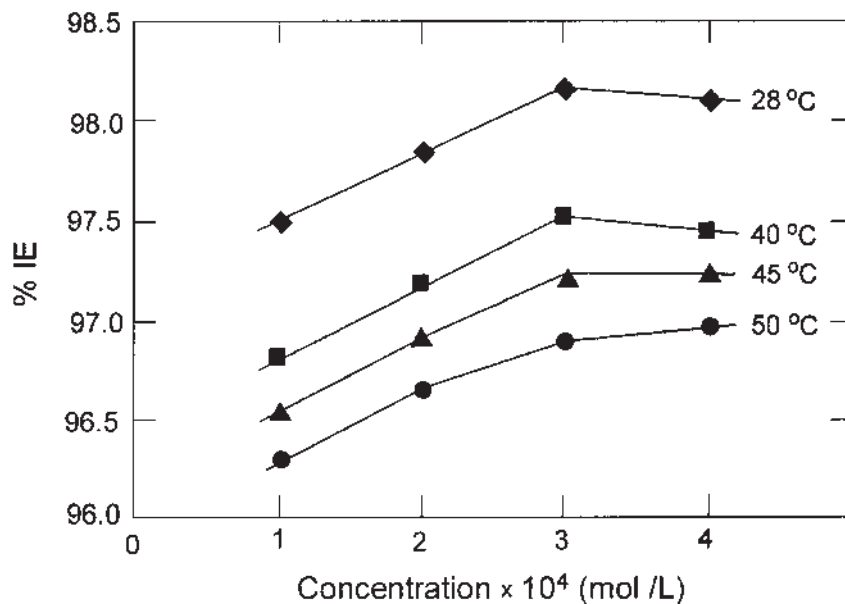


Fig. 4. Variation of the inhibition efficiency with the concentration of inhibitor in 0.1 M HCl.

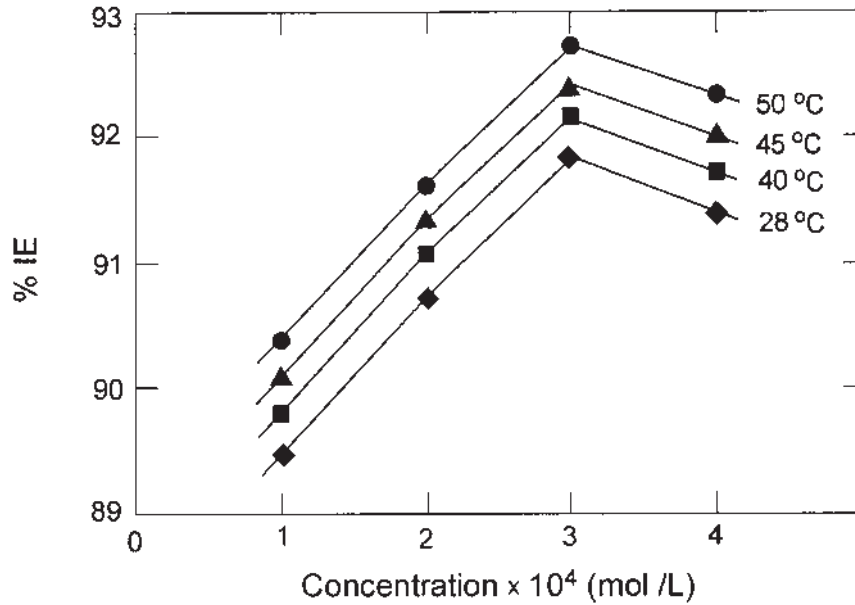


Fig. 5. Variation of the inhibition efficiency with the concentration of inhibitor in 0.05 M H₂SO₄.

The effect of the temperature on the *IE* is shown in Figs. 6 and 7. The % of *IE* of the compound did not change significantly with increasing temperature in the range from 28 to 50 °C in both acid solutions. This is a clear indication that the investigated compound works more effectively at lower temperatures in both acid media. It was also observed that the inhibition power of PFTU in reducing the cor-

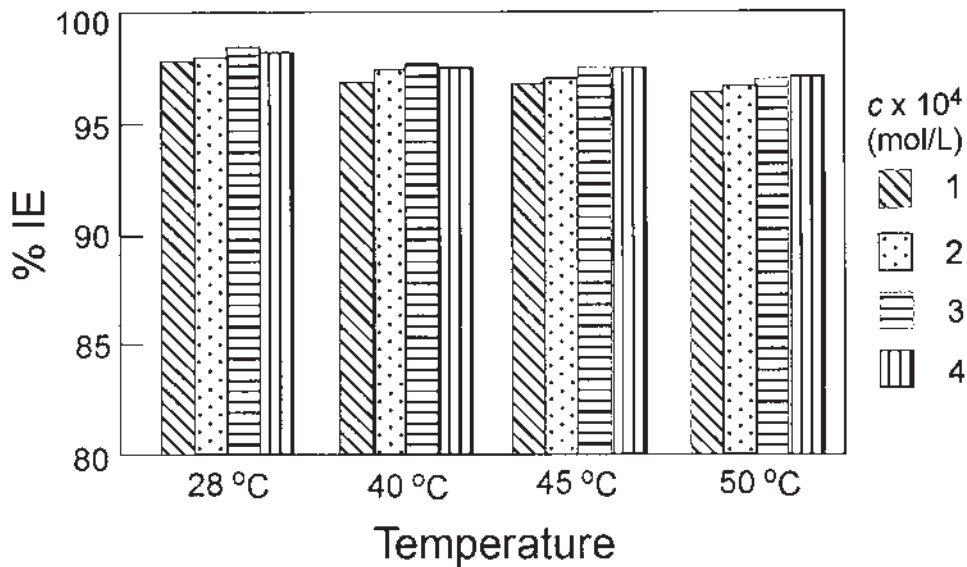


Fig. 6. The effect of temperature on *IE* in 0.1 M HCl.

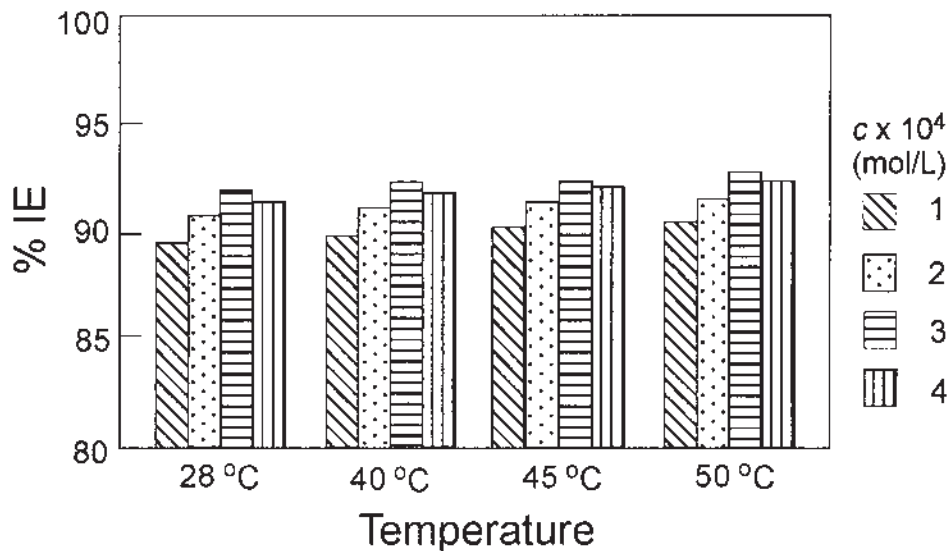


Fig. 7. The effect of temperature on *IE* in 0.05 M H₂SO₄.

rosion of mild steel in sulphuric acid was less than in hydrochloric acid. The high *IE* exhibited by the compound may be attributed to its adsorption on the metal surface through polar groups as well as through π -electrons of the double bond. This leads to a greater coverage of the metal surface by the compound which results in a higher *IE*. It is evident from the results that FPTU is not temperature sensitive in HCl medium, while it is in lower concentrations of H₂SO₄.

TABLE III. Activation energy (E_a) and Gibbs energy of adsorption (ΔG_{ads}) for mild steel in 0.1 M HCl and 0.05 M H₂SO₄ at different temperatures

| Acid solution | $c(\text{FPTU}) \times 10^4$ mol/L | E_a kJ mol ⁻¹ | $-\Delta G_{ads}/\text{kJ mol}^{-1}$ | | | |
|---------------------------------------|---------------------------------------|-------------------------------|--------------------------------------|-------|-------|-------|
| | | | 28 °C | 40 °C | 45 °C | 50 °C |
| 0.1 M HCl | 0 | 33.69 | – | – | – | – |
| | 1 | 39.73 | 42.08 | 43.10 | 43.58 | 44.07 |
| | 2 | 42.18 | 40.76 | 41.65 | 42.06 | 42.50 |
| | 3 | 44.92 | 40.15 | 40.92 | 41.26 | 41.62 |
| | 4 | 43.22 | 39.34 | 40.11 | 40.53 | 40.92 |
| 0.05 M H ₂ SO ₄ | 0 | 29.48 | – | – | – | – |
| | 1 | 26.78 | 38.27 | 39.88 | 40.61 | 41.34 |
| | 2 | 26.27 | 36.89 | 38.47 | 39.18 | 39.89 |
| | 3 | 26.06 | 36.22 | 37.78 | 38.48 | 39.20 |
| | 4 | 26.16 | 35.37 | 36.88 | 37.58 | 38.29 |

The values of the Gibbs energy of adsorption (ΔG_{ads}) and the equilibrium constant (K) at different temperatures were calculated using the following equations:

$$\Delta G_{\text{ads}} = -RT \ln (55.5K) \quad (4)$$

$$K = \theta / (c (1 - \theta)) \quad (5)$$

where R is the gas constant and 55.5 is the concentration of water in mol/L and θ is the degree of surface coverage of the metal surface, and c is the concentration of inhibitor in mol/L. The negative values of ΔG_{ads} (Table III) indicates spontaneous adsorption of the inhibitor on the mild steel surface. The negative values of ΔG_{ads} also suggest strong interaction of the inhibitor molecules with the mild steel surface.^{19,20} The ΔG_{ads} values (Table III) for the studied compound in 0.1 M HCl at higher temperatures were larger than 40 kJ/mol, indicating that the compound is chemisorbed on the mild steel surface,^{22,23} while in H_2SO_4 medium, physical or mixed adsorption of the inhibitor molecules was observed.

The values of the activation energy (E_a) were calculated using the Arrhenius equation^{23,24}

$$\ln (r_2 / r_1) = -E_a \Delta T / (R T_2 T_1) \quad (6)$$

where r_1 and r_2 are the corrosion rates at temperature T_1 and T_2 , respectively, and ΔT is the difference in temperature ($T_1 - T_2$). The inhibition efficiency and the degree of surface coverage change with temperature; this change is incorporated in the values of the activation energy. θ and IE are more sensitive to temperature changes, when the differences in activation energy between the inhibited and uninhibited solutions are larger.²⁵ The higher values of E_a in the inhibited solution of HCl indicate that FPTU is more effective at lower temperatures.²⁶ However, in H_2SO_4 medium, the values of E_a were less than that of the uninhibited system; thus indicating that the investigated compound was also more effective at temperatures above 50 °C.

CONCLUSIONS

1. FPTU acts as an efficient anodic inhibitor for the corrosion of mild steel in both HCl and H_2SO_4 acid solutions.
2. FPTU inhibit the corrosion of mild steel by adsorption on the metal surface.
3. The inhibitive power of FPTU in reducing corrosion loss of mild steel in HCl is comparatively higher than in H_2SO_4 medium.
4. FPTU forms a chemisorbed film on the mild steel surface in HCl medium, whereas in H_2SO_4 , the inhibition is governed by the physisorption or mixed adsorption mechanism.

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ИЗВОД

ИНХИБИЦИОНО ДЕЈСТВО *N*-ФУРФУРИЛ-*N'*-ФЕНИЛТИОУРЕЕ НА
КОРОЗИЈУ ЧЕЛИКА У КИСЕЛОЈ СРЕДИНИS. DIVAKARA SHETTY¹, PRAKASH SHETTY^{2*} и H. V. SUDHAKER NAYAK³¹Department of Mechanical Engineering, Manipal Institute of Technology, Manipal 576 104, ²Department of Chemistry, Manipal Institute of Technology, Manipal 576 104, India и ³Department of Metallurgical and Materials Engineering, National Institute of Technology, Suratkal, Srinivasnagar 575 025, India

Инхибиционо дејство *N*-фурфурил-*N'*-фенилтиоуреа (FPTU) на корозију челика у воденом раствору 0,05 и 0,1 М HCl као и 0,025 и 0,05 М H₂SO₄ је показано потенциодинамичком поларизационом техником. Поларизациони подаци су показали да FPTU делује као ефикасни анодни инхибитор за челик у растворима обе киселине. Веома висока инхибиција је уочена у растворима обе киселине и утврђено је да зависи од концентрације инхибитора и температуре. Кинетички параметри адсорпције указују на спонтану адсорпцију и јаку интеракцију FPTU са површином челика.

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