

The Effect of Temperature on the Adsorption Behavior and Inhibition Performance of a Pyrimidine-Type Inhibitor at Medium Temperature Range (25°C to 80°C)

Yi He, Shuai Ren, Xi Wang, David Young, Marc Singer
Institute for Corrosion and Multiphase Technology
Department of Chemical and Biomolecular Engineering
Ohio University
342 West State Street
Athens, OH 45701, USA

Maalek Mohamed-Saïd
TotalEnergies
OneTech - CSTJF, Avenue Larribau
F-64018 Pau
France

Sheyla Camperos
TotalEnergies
OneTech - TRTG - TotalEnergies Research &
Technology Gonfreville
BP 27 76 700 Harfleur – FRANCE

ABSTRACT

In the oil and gas industry, long-distance transmission of produced hydrocarbons is usually carried out in large-diameter steel pipelines. However, water co-produced with the oil and gas, combined with CO₂ or H₂S, can cause severe corrosion of internal pipeline surfaces. A widely applied, economically effective method of corrosion control is to inject corrosion inhibitors (CIs). Adsorption of the organic molecules on surfaces through heteroatom functionalities, containing nitrogen, oxygen, sulfur and/or phosphorus, can markedly change the corrosion resistance characteristics of the exposed metal, typically mild steel for pipelines. Among these organic compounds, heterocyclic molecules containing nitrogen atoms have been demonstrated to be excellent corrosion inhibitors (CIs) for many alloys in various aggressive media. In this research, surface saturation concentrations, as well as inhibition efficiencies of tetradecyltetrahydropyrimidinium (THP-C14), were determined at 25, 55 and 80°C by monitoring linear

© 2022 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.

Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

polarization resistance (LPR) until the corrosion of the steel specimens stabilized. Potentiodynamic sweeps were obtained at the end of each test. The five most frequently used adsorption isotherms, which correlate coverage and inhibitor concentration using different assumptions, were reviewed and adapted to fit the corrosion inhibition behavior. These isotherms were evaluated based on their goodness of fit and the relevance of their underlying assumptions. In addition, the equilibrium constants of adsorption/desorption (K_{AD}) at 25, 55 and 80°C were determined by fitting the steady state experimental data. Finally, the changes of activation energy with and without inhibitor at 25, 55 and 80°C were calculated and compared.

Keywords: corrosion inhibitors, inhibition efficiency, surface saturation concentration, adsorption isotherms, changes of activation energy

INTRODUCTION

In the oil and gas industry, long-distance transportation of petroleum and related products is usually carried out in large-diameter carbon steel pipelines. Water present with the oil, along with corrosive species such as CO_2 , H_2S and organic acids, causes severe corrosion of the inner pipe walls.¹ An effective method of controlling corrosion is to continuously inject corrosion inhibitors into pipelines conveying oil-water mixtures. As corrosion occurs on water wetted metal surfaces, corrosion inhibitor (CI) molecules form protective films which retard electrochemical reaction rates at the water-metal interface,² thereby protecting carbon steel pipes against CO_2 ("sweet") corrosion and H_2S ("sour") corrosion. Most commercial CIs are a complex mixture of several compounds that contain surfactant-type active ingredients, such as imidazoline, amine, phosphate ester, and quaternary ammonium derivatives.³ Adsorption of organic molecules on surfaces through heteroatom functionalities, containing nitrogen, oxygen, sulfur and/or phosphorus, can markedly change the corrosion resistance properties of metals. Among these organic compounds, heterocyclic molecules containing nitrogen atoms have been demonstrated to be excellent corrosion inhibitors (CIs) for many metals and alloys in various aggressive media.⁴⁻⁶ The performance of quaternary ammonium-type, imidazolinium-type and thiol-type corrosion inhibitor model compounds is the focus of intense study⁷⁻¹⁰ in order to deliver descriptive and predictive inhibition models, as well as inhibitor testing methodologies, for industrial users of these compounds.

The goal of the current research is to develop an inhibitor testing protocol and to develop an accurate inhibition prediction tool. Experiments that cover a range of experimental conditions, including inhibitor concentrations and temperatures, are being undertaken. These will enable the determination of fundamental corrosion inhibition parameters as the inputs for an electrochemical model aimed at facilitating the prediction of inhibitor performance, at any given CI concentration and for a broad range of experimental conditions. This research also investigated the use of different adsorption isotherms to correlate coverage and inhibitor concentration at different temperatures.

Corrosion Inhibition at Elevated Temperatures

The available literature on the effect of temperature on inhibition efficiency can appear contradictory. Ding, *et al.*¹¹ performed a series of experiments in a standard 2L glass cell at low to medium temperature (25°C, 50°C and 80°C) to characterize adsorption kinetics, using imidazoline-type and quat-type inhibitors. These experiments included general corrosion inhibition tests using linear polarization resistance (LPR) measurements and direct determination of adsorption behavior using a quartz crystal

© 2022 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.

Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

microbalance (QCM). Both test methods yielded similar trends for the two inhibitors tested. This suggested that the loss of inhibition efficiency as temperature increased was a result of desorption being favored at higher temperatures. However, Bentiss, *et al.*¹² studied the role of a thiadiazole-type inhibitor on the corrosion behavior of mild steel in an acidic environment at different temperatures (30°C-60°C). They found that the efficiency of the inhibitor increased with temperature and attributed the temperature dependency as a sign of chemical adsorption; indicating that the chemical adsorption is more favorable than physical adsorption at the higher temperature. However, there was no further discussion on what correlates the temperature dependent behavior with the nature of chemisorption. Zhang, *et al.*^{13, 14} examined the inhibition performance of three different halogen-substituted imidazoline derivatives (labeled as 1-IM, 2-IM, 3-IM) for mild steel in a hydrochloric acid solution from 30°C to 70°C. They noticed that the performance of the two inhibitors either decreased (1-IM, 3-IM) or only slightly changed (2-IM) at elevated temperatures. The authors concluded that these three inhibitors are mainly physisorbed on metal surfaces. The dominance of chemisorption or physisorption depends upon the chemistry (brine, Cl molecules and metallic surface charge), it is not only temperature dependent.

Understanding the role of high temperature on inhibition performance is a complex task. The understanding of the corrosion inhibition mechanism at low temperatures serves as a solid foundation for research at higher temperatures. However, the role of temperature on corrosion inhibition is complex and differs from inhibitor to inhibitor. In addition, the understanding of the effect of temperature on inhibitor adsorption behavior is also limited. Therefore, the work in this paper is limited to adsorption, *i.e.*, excluding thermal degradation effects (if any).

Fitting of Different Adsorption Isotherms

In consideration of the several adsorption isotherms that are available, a proper model should be chosen to describe the adsorption and desorption process of THP-C14 molecules on the steel surface in the studied conditions. In this section, five adsorption isotherm models will be evaluated by fitting the steady state experimental data (C_{inh} vs. θ_{eq}). From the coefficient of determination (R^2) of fitting, the relative adequacy of these models to studied adsorption processes can then be discussed.

Before discussing the fitting results, the five utilized adsorption isotherm models are introduced, *i.e.*, the Langmuir, Temkin, Frumkin and Flory-Huggins/Dhar-Flory-Huggins models.

- (a) Langmuir model: Homogeneous surface, monolayer, and no interaction between adsorbed inhibitor molecules. When the adsorption-desorption process of the corrosion inhibitor has reached a point where the coverage remains unchanged with respect to time:¹⁵

$$C_{inh}K_{AD} = \left(\frac{\theta_{eq}}{1 - \theta_{eq}} \right) \quad (1)$$

Where θ_{eq} is the steady state surface coverage values at precise Cl concentrations. K_{AD} is the equilibrium constant of adsorption/desorption, which is equal to the ratio of the adsorption and desorption constants. C_{inh} is the bulk concentration of the Cl.

- (b) Temkin model: Heterogeneous surface, no molecular interactions, considering the surface is made up of a great number of small patches, on each of which the Langmuir isotherm is applicable.¹⁶

$$\theta_{eq} = \frac{1}{g} \ln (K_{AD} C_{inh}) \quad (2)$$

Where g is the adsorbent-adsorbate interaction constant.

- (c) Frumkin model: Heterogeneous surface, considering lateral interactions between adsorbed surfactant molecules.¹⁶

$$K_{AD} C_{inh} = \frac{\theta_{eq}}{1 - \theta_{eq}} \exp (-f \theta_{eq}) \quad (3)$$

Where f is a constant relating to the interactions between adsorbate molecules and is independent of θ . The Langmuir model is a specific case of Frumkin model with $f=0$.

- (d) Flory-Huggins/Dhar-Flory-Huggins model: Considers the substitution of adsorbed solvent by adsorbing molecules.¹⁶ Different from the Flory-Huggins model, the Dhar-Flory-Huggins isotherm has one exponential factor. Strictly, it is incorrect to refer to an isotherm containing the configurational term $\frac{\theta_{eq}}{\delta(1-\theta_{eq})^\delta}$, which is related to the arrangement of atom/molecules on the metal surface, as the “Flory-Huggins isotherm”, since Flory-Huggins statistics leads to an isotherm having a different form for the configurational term, which is $\exp(\delta - 1)$.

$$\text{Flory-Huggins:} \quad K_{AD} C_{inh} = \frac{\theta_{eq}}{\delta(1-\theta_{eq})^\delta} \quad (4)$$

$$\text{Dhar-Flory-Huggins:} \quad K_{AD} C_{inh} = \frac{\theta_{eq}}{e^{(\delta-1)}(1-\theta_{eq})^\delta} \quad (5)$$

Where δ is the number of solvent molecules substituted by an adsorbate molecule. The Langmuir model is a specific case of Flory-Huggins/Dhar-Flory-Huggins model with $\delta=1$.

By fitting the experimental data with these non-linear equations, the constants in these equations were determined and the fitting curves were plotted together with experimental data for comparison.

Changes of Activation Energy

Dominguez, *et al.*^{9,17}, have discussed the physical interpretation of the chemical component of the total activation energy in the electrochemical dissolution of steel. The effect of the alkyl tail length on the kinetics of the electrochemical process behind CO₂ corrosion of a UNS K03014 steel at pH 4.0 was investigated. The activation energy associated with the corrosion process was determined *via* an Arrhenius plot from charge transfer resistance measurements at the potential of zero charge (PZC). It was assumed that the rate constant of the iron dissolution was governed by the chemical component of the activation energy. This method^{9,17} used to obtain the difference in activation energy between uninhibited and maximum inhibited conditions, could be simplified since what the inhibition model needs are the activation energy differences between inhibited and uninhibited environments, which does not have to be evaluated at the PZC. Consequently, a new method has been proposed to obtain the activation energy change directly from the potential polarization curve. At a fixed potential, the difference in chemical activation energy can still be determined by the difference in total activation energy. In this paper, surface saturation concentration (C_{inh}) will be obtained by monitoring changes of corrosion rate with time in the electrolyte with different inhibitor concentrations.

The current densities in uninhibited (i_{un}) and maximum inhibited conditions ($i_{inh, max}$) can be represented by the following equations, considering the anodic current:

$$i_{un} = A \exp\left(-\frac{\Delta G_{un}^{\#}}{RT}\right) \exp\left(\frac{\alpha n F \eta}{RT}\right) \quad (6)$$

$$i_{inh, max} = A \exp\left(-\frac{\Delta G_{inh, max}^{\#}}{RT}\right) \exp\left(\frac{\alpha n F \eta}{RT}\right) \quad (7)$$

Where $A = nF C_R^s \frac{k_B T}{h}$, n is number of electrons transferred per mole; C_R^s is the concentration of a reactant at the metal-solution interface; k_B is the Boltzmann constant; h is the Planck constant; $\Delta G_{un}^{\#}$ is the activation energy without inhibitor at reversible potential (E_{rev}), and $\Delta G_{inh, max}^{\#}$ is the activation energy in maximum inhibited condition; and η is overpotential, the difference between applied potential and reversible potential ($E - E_{rev}$). F is the Faraday constant. R is the ideal gas constant, and T is the absolute temperature in Kelvin (K).

Considering the ratio of these two current densities:

$$i_{un}/i_{inh, max} = \exp\left(-\frac{\Delta G_{un}^{\#}}{RT}\right) / \exp\left(-\frac{\Delta G_{inh, max}^{\#}}{RT}\right) \quad (8)$$

Applying the natural logarithm on both sides of the above equation and rearranging yields:

$$\Delta G_{inh, max}^{\#} - \Delta G_{un}^{\#} = RT \ln (i_{un}/i_{inh, max}) \quad (9)$$

The above equation indicates that the activation energy difference between uninhibited and maximum inhibited conditions ($\Delta G_{inh, max}^{\#} - \Delta G_{un}^{\#}$) can be determined by the ratio of their corresponding current densities ($i_{un}/i_{inh, max}$), as long as the process is charge transfer controlled.

This paper is specifically related to the characterization of a model compound possessing a pyrimidine structural moiety (tetradecyl-1,4,5,6-tetrahydropyrimidinium, or THP-C14), which is found in particular commercial CI formulations; its synthesis and characterization as a model compound is reported elsewhere.¹⁸ The scope of work not only involves the corrosion inhibition performance of selected corrosion inhibitor but also the investigation of adsorption behavior. In this research, surface saturation concentrations as well as inhibition efficiencies at 25, 55 and 80°C were determined by monitoring linear polarization resistance (LPR) until the corrosion of the steel specimens stabilized. Potentiodynamic sweeps were obtained at the end of each test. The five most frequently used adsorption isotherms, which correlate coverage and inhibitor concentration using different assumptions, are reviewed and adapted to fit the corrosion inhibition behavior of tetradecyltetrahydropyrimidinium (THP-C14). These isotherms were evaluated based on their goodness of fit and the relevance of their underlying assumptions. In addition, the equilibrium constants of adsorption/desorption (K_{AD}) at 25, 55 and 80°C were determined by fitting the steady state experimental data. Finally, the changes of activation energy with and without inhibitor at 25, 55 and 80°C were calculated and compared.

EXPERIMENTAL METHODOLOGY

Materials and Chemicals

© 2022 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.

Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).