

Effect of Corrosion Inhibitor Alkyl Tail Length on the Electrochemical Process Governing CO₂ Corrosion of Mild Steel

Juan Dominguez Olivo,^{‡,*} Bruce Brown,^{*} David Young,^{*} and Srdjan Nešić^{*}

Four different model compounds were synthesized and utilized in this research to relate inhibitor alkyl tail length to changes in the activation energy of the electrochemical process associated with CO₂ corrosion of an API 5L X65 steel at pH 4.0. The molecular structure of the model compounds was composed of the same head group, dimethyl-benzyl ammonium, with four different alkyl tail lengths corresponding to butyl (-C₄H₉), octyl (-C₈H₁₇), dodecyl (-C₁₂H₂₅), and hexadecyl (-C₁₆H₃₃). In data analysis, the chemical component of the total activation energy was calculated using an Arrhenius-type relationship and by working at the potential of zero charge (PZC). A linear relationship between the tail length of the corrosion inhibitor and the change in the activation energy of the corrosion electrochemical process was determined, suggesting that the tail modifies the activation energy of the electrochemical process underlying CO₂ corrosion.

KEY WORDS: activation energy, alkyl tail length, corrosion inhibitors, CO₂ corrosion, mitigation

INTRODUCTION

A corrosion inhibitor is a chemical substance that can significantly reduce corrosion, in certain environments, when added in small concentrations.¹ The oil and gas industry typically uses organic surfactant-type compounds such as amines, amides, and imidazolines, which primarily function by adsorbing on the metal surface and forming a "barrier" against corrosion.¹ Regarding the effect of the alkyl tail length of the corrosion inhibitors, there have been studies relating the alkyl tail with the mitigation efficiency of the corrosion inhibitors.¹⁻⁶ In general, it was concluded that the longer the corrosion inhibitor alkyl tail, the greater the corrosion mitigation efficiency. However, the key link between inhibitor alkyl tail length and corrosion mitigation is not properly established.

Consequently, the main purpose of this research is to propose a model that better describes the inhibition process and account for the effect of the alkyl tail length mechanistic role.

EXPERIMENTAL PROCEDURES

2.1 | Synthesis of Corrosion Inhibitor Model Compounds

To be able to effectively isolate the effect of the alkyl tail length of the corrosion inhibitors, four different model compounds were synthesized in-house and tested against CO₂ corrosion of mild steel. The model compounds consisted of the same head group, dimethyl-benzyl-ammonium (denoted heretofore as "Q"), with four different alkyl tail lengths: butyl (-C₄H₉), octyl (-C₈H₁₇), dodecyl (-C₁₂H₂₅), and hexadecyl

(-C₁₆H₃₃). The general synthesis reaction is as depicted in Figure 1.

2.2 | Electrochemical Experiments

A three-electrode glass cell setup was used to perform corrosion and corrosion mitigation experiments at 1 bar (100 kPa), pH 4.0, and 30, 35, 40, and 45°C with a 1 wt% NaCl electrolyte; an API 5L X65 steel (UNS K03014⁽¹⁾; Fe 97.7, C 0.13, Mn 1.16, Mo 0.16, wt%) rotating cylinder electrode (RCE) at 1,000 rpm was used as the working electrode. A platinum covered titanium mesh was used as a counter electrode and an Ag/AgCl (KCl saturated) electrode was used as the reference. CO₂ was used for purging the system and the solution pH was adjusted and maintained at pH 4.0±0.1 during each experiment. Linear polarization resistance (LPR) measurements were taken to obtain the charge transfer resistance by polarizing the working electrode ±5 mV from the corrosion potential. Corrosion rates were then calculated by using a B value of 26 mV/decade. Electrochemical impedance spectroscopy (EIS) measurements were taken at applied bias potentials between -0.85 V_{Ag/AgCl} and -0.5 V_{Ag/AgCl} using a frequency range between 10 mHz to 5 kHz. Effective double layer capacitances were obtained by the method formulated by Hirschorn, et al., as described elsewhere.⁷ The potential of zero charge (PZC) was found via the minimum capacitance method.⁸ Corrosion inhibitors were tested at the surface saturation concentration (the minimum concentration that yielded the maximum efficiency of a corrosion inhibitor) with values reported and described elsewhere.⁹

Submitted for publication: October 17, 2018. Revised and accepted: December 13, 2018.

Preprint available online: December 13, 2018, <https://doi.org/10.5006/3076>. Recipient of first place in the Marcel Pourbaix Corrosion Science category in the Student Poster Session at CORROSION 2018, April 2018, Phoenix, Arizona.

[‡] Corresponding author. E-mail: jd616112@ohio.edu.

^{*} Institute for Corrosion and Multiphase Technology, Dept. of Chemical and Biochemical Eng., Ohio University, 342 W State St., Athens, OH 45701.

⁽¹⁾ UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.

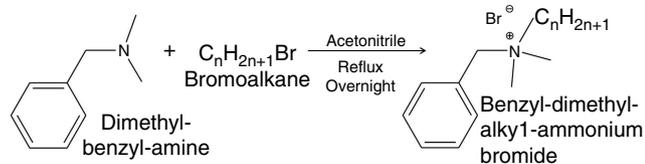


FIGURE 1. General reaction for the model compounds utilized as corrosion inhibitors.

RESULTS AND DISCUSSION

At the outset, it was assumed that at surface saturation concentration the adsorbed organic inhibitor forms a uniform film that affects both components of the electrochemical activation energy: the chemical and the electrical component. To separate the two, the chemical activation energies were found at the potential of zero charge (PZC). This was done based on an assumption that the electrical component of the activation energy was minimized at the PZC⁹ so that the rate constant of the process obtained via an Arrhenius plot was dominated by the chemical component. It was also assumed that the corrosion rate was inversely proportional to the polarization resistance (according to the Stern-Geary equation¹⁰⁻¹¹).

3.1 | Effect of Alkyl Tail Length on Activation Energy

Dominguez, et al.,⁹ have discussed the physical interpretation of the chemical component of the total activation energy in the electrochemical dissolution of steel. The activation energy associated with the corrosion process was

determined via an Arrhenius plot from charge transfer resistance measurements at the PZC. It was assumed that the rate constant of the iron dissolution was governed by the chemical component of the activation energy. The logarithm of the charge transfer resistance was plotted versus the inverse of the absolute temperature. Figure 2(a) shows the Arrhenius plot for a CO₂ system with no corrosion inhibitor. The activation energy was determined to be ca. 47 kJ/mol (5,695 K × 8.314 J/mol·K ≈ 47 kJ/mol). Because no clear PZC was detected in the presence of corrosion inhibitors, the activation energies were determined at the PZC in the absence of corrosion inhibitors (-450 mV_{SHE}). The purpose was to compare the activation energy changes, similarly to the method proposed by Gileadi, et al.¹² Figure 2(b) shows the Arrhenius plot for a CO₂ system with Q-C12 corrosion inhibitor model compound. The activation energy was determined to be ca. 54 kJ/mol. From these figures, it can be observed that the addition of a corrosion inhibitor increased the activation energy of the electrochemical process underlying corrosion.

The activation energies for the CO₂ corrosion process in the presence of the adsorbed corrosion inhibitor model compounds were plotted against their respective alkyl tail lengths (calculated with an advanced molecule editor software¹³). The plot of the activation energies vs. model compound alkyl tail length is shown in Figure 3. The plot showed a linear relationship between the activation energy and the increase of the inhibitor tail length. In addition, if the resulting graph is extrapolated to “zero-length” alkyl tail, the result is ca. 48.5 kJ/mol, which is very close to the activation energy in the absence of corrosion inhibitors (46.9 ± 1.8 kJ/mol). This result suggests that the role

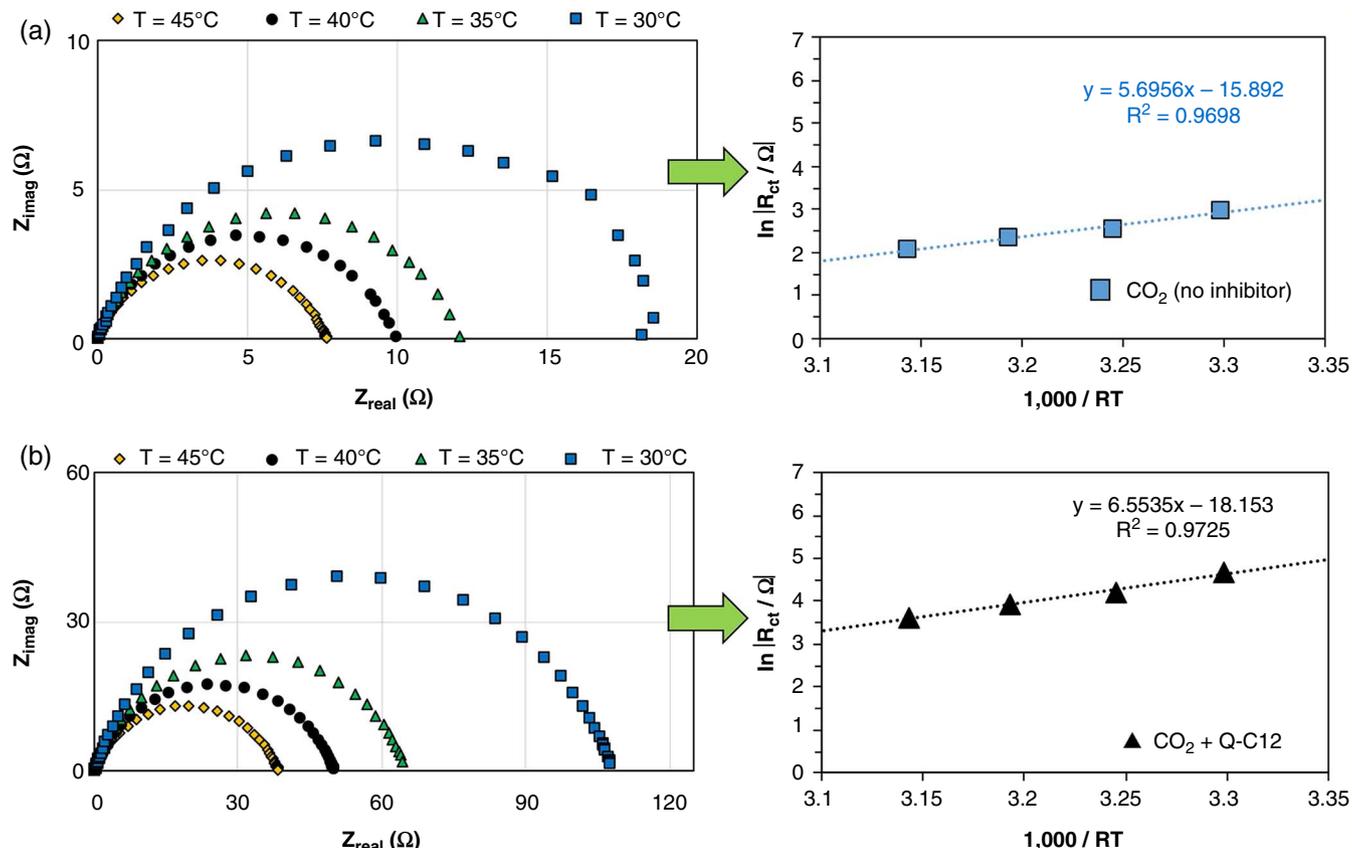


FIGURE 2. (a) Determination of activation energy in a CO₂ system with no inhibitor (46.9 ± 1.8 kJ/mol). (b) Determination of activation energy in the presence of the inhibitor model compound Q-C12 (53.8 ± 1.5 kJ/mol).

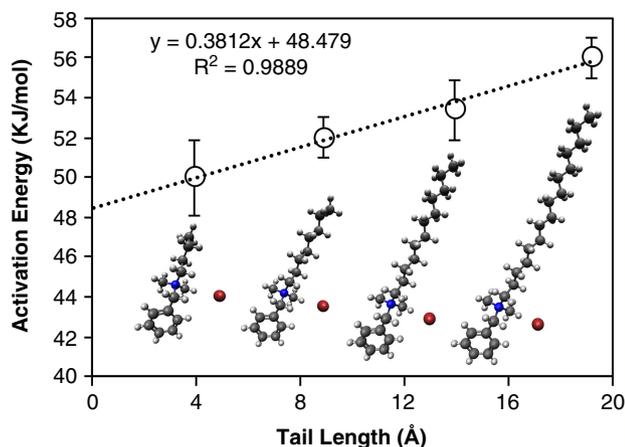


FIGURE 3. Activation energies of inhibited CO₂ corrosion electrochemical processes vs. inhibitor alkyl tail length.

of the head group in the quaternary ammonium model compounds is primarily to attach to the metal surface and the alkyl tail length is responsible for modifying the chemical activation energy of the electrochemical process underlying CO₂ corrosion. The observed increase in activation energy can plainly be explained by the influence of the hydrophobic non-polar inhibitor alkyl tail on charge transfer resistance, as it repels water more effectively when its length increases. Due to the "dilution" and displacement of water by the adsorbed inhibitor molecules at the metal surface, the ionization activation energy of the metal increases and, as a result, the anodic dissolution of iron proceeds at a lower rate.

CONCLUSIONS

- The activation energy of the electrochemical processes underlying CO₂ corrosion was obtained for each inhibitor model compound at their respective surface saturation concentration. The longer the tail, the larger the increase in activation energy.
- Increase in activation energy was consistent with corrosion rate results. The longer the alkyl tail length, the greater the

corrosion mitigation efficiency for the homologous series evaluated.

- The results suggested that the main role of the head group of the quaternary ammonium model compounds is to help attach the inhibitor molecule to the metal surface, while the hydrophobicity of the alkyl tail plays a governing role in the inhibition process by displacing water molecules from the surface and increasing the chemical activation (ionization energy) for metal dissolution.

ACKNOWLEDGMENTS

The authors would like to thank the following companies for their financial support: Anadarko, Baker Hughes, BP, Chevron, CNOOC, ConocoPhillips, DNV GL, ExxonMobil, M-I SWACO (Schlumberger), Multi-Chem (Halliburton), Occidental Oil Company, Petrobras, PTT, Saudi Aramco, Shell Global Solutions, SINOPEC (China Petroleum), TransCanada, TOTAL, and Wood Group Kenny.

References

1. V.S. Sastri, *Green Corrosion Inhibitors*, 2nd ed. (Hoboken, NJ: John Wiley & Sons, 2011).
2. M. Palomar-Pardavé, M. Romero-Romo, H. Herrera-Hernández, M.A. Abreu-Quijano, N.V. Likhanova, J. Uruchurtu, J.M. Juárez-García, *Corros. Sci.* 54 (2012): p. 231-243.
3. E. McCafferty, N. Hackerman, *J. Electrochem. Soc.* 119 (1972): p. 146.
4. A. Edwards, C. Osborne, S. Webster, D. Klenerman, M. Joseph, P. Ostovar, M. Doyle, *Corros. Sci.* 36 (1994): p. 315-325.
5. W.J. Lorenz, F. Mansfeld, *Electrochim. Acta* 31 (1985): p. 467-476.
6. C. Cao, *Corros. Sci.* 38 (1996): p. 2073-2082.
7. B. Hirschorn, M.E. Orazem, B. Tribollet, V. Vivier, I. Frateur, M. Musiani, *Electrochim. Acta* 55 (2010): p. 6218-6227.
8. P. Delahay, *Double Layer and Electrode Kinetics* (Hoboken, NJ: John Wiley & Sons Inc, 1965).
9. J.M. Dominguez Olivo, D. Young, B. Brown, S. Nestic, "Effect of Corrosion Inhibitor Alkyl Tail Length on the Electrochemical Process Underlying CO₂ Corrosion of Mild Steel," CORROSION 2018, paper no. 11537 (Houston, TX: NACE International, 2018), p. 1-15.
10. M. Stern, *J. Electrochem. Soc.* 104 (1957): p. 53-63.
11. W.J. Lorenz, F. Mansfeld, *Corros. Sci.* 21 (1981): p. 647-672.
12. E. Gileadi, *Electrosorption*, 1st ed. (New York, NY: Springer, 1967).
13. M.D. Hanwell, D.E. Curtis, D.C. Lonie, T. Vandermeersch, E. Zurek, G.R. Hutchison, *J. Cheminform.* 4 (2012): article id 4:17.