The Effects of Organic Compounds on Inhibition of Hydrogen Permeation Through a Mild Steel Membrane

H. A. Duarte  
*University of South Carolina - Columbia*

D. M. See  
*University of South Carolina - Columbia*

Branko N. Popov  
*University of South Carolina - Columbia*, popov@engr.sc.edu

Ralph E. White  
*University of South Carolina - Columbia*, white@cec.sc.edu

Follow this and additional works at: [https://scholarcommons.sc.edu/eche_facpub](https://scholarcommons.sc.edu/eche_facpub)  
Part of the Chemical Engineering Commons

**Publication Info**  
© The Electrochemical Society, Inc. 1997. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in the Journal of the Electrochemical Society.  
http://www.electrochem.org/  
Publisher's link: [http://dx.doi.org/10.1149/1.1837810](http://dx.doi.org/10.1149/1.1837810)  
DOI: 10.1149/1.1837810

This Article is brought to you by the Chemical Engineering, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact digres@mailbox.sc.edu.
The Effects of Organic Compounds on Inhibition of Hydrogen Permeation Through a Mild Steel Membrane

H. A. Duarte,* D. M. See, B. N. Popov,** and R. E. White**

Department of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29208, USA

ABSTRACT

The effectiveness of 5-(4-pyridyl)-2,7-norbornadiene, and 1 phenyl-2-propynol (PP) on inhibition of the hydrogen evolution reaction on a 1010 steel membrane and on the degree of hydrogen ingress into the membrane was determined. Hydrogen evolution rates and permeation currents were monitored as a function of time at different applied potentials. In the presence of 0.5 g/liter PP in the electrolyte, the hydrogen discharge and permeation current density were inhibited by 98 and 95%, respectively.

Introduction

Hydrogen can cause embrittlement of metals and alloys during electroplating, cathodic protection, and corrosion of metals. Various method have been proposed to decrease hydrogen embrittlement. However, it is usually impossible to reduce hydrogenation of metals and alloys to a level that eliminates the possibility of hydrogen cracking. According to our earlier studies, an alloy surface modification with underpotentially deposited metals (Zn, Bi, Pb) or deposited Zn or Bi inhibits the hydrogen discharge reaction and reduces drastically the degree of hydrogen ingress in the substrate.

Corrosion inhibitors were also used to decrease the hydrogen permeation and embrittlement effects. Martin found that all three states of H in steels, mobile, reversibly trapped, and irreversibly trapped were minimized in quantity when inhibitors were used to mitigate corrosion. According to Wilhelm et al., diamines with long carbon chains were most effective in reducing the corrosion rate and hydrogen adsorption.

The objective of this study was to investigate the effect of two organic compounds 1-phenyl-2-propyn-1-ol (PP) and 5-(4-pyridyl)-2,7-norbornadiene (PN) on the hydrogen permeation through a mild steel membrane.

Experimental

The Devanathan-Stachurski permeation technique was used to investigate the rate of hydrogen permeation through a 1010 steel with an area of approximately 0.4 cm². Prior to the experiment, the membrane was prepared by polishing with 0.5 µm high purity alumina powder and cleaning in an ultrasonic cleaning bath. Just prior to placing the membrane in the permeation cell, it was etched for 20 s in a methanol solution containing 1% H₂SO₄, rinsed with deionized water, and then dried in the air.

The electrolyte on the cathodic side of the cell was 0.5 M HCl. The rate of hydrogen permeation through the alloy in the absence and presence of 0.5 g/liter of PN or PP was recorded continuously as a function of time. The electrolyte on the anodic side of the cell was 0.2 M NaOH. To keep electrolyte impurities at the lowest possible level, the solutions for the anodic and cathodic compartments were pre-electrolyzed at least 24 h in a separate electrolytic cell prior to introduction into the compartment. The potential of the "diffusion side" of the membrane (the side from which the hydrogen emerged) was set at a value that corresponded to a practically zero concentration of the absorbed atomic hydrogen on the surface. This condition was maintained by the instantaneous ionization of all hydrogen atoms that diffused through the membrane and emerged on the diffusion side.

To avoid passivation or dissolution of the metal, the anodic side of the steel membrane was always electroplated with a thin layer (0.15 to 0.2 µm) of palladium. It was assumed in this work that this thin film of palladium would not affect the permeation rate of hydrogen through the steel membrane because it is well known that hydrogen diffuses rapidly through palladium. The deposition was carried out in an electrolyte containing 2 X 10⁻⁶ M sodium tetrathiotetrapalladium ([Na₂Pd(NO₂)₄]), using a current density of 200 μA/cm² for 4 h. Then, the electrolyte was drained off, and the compartment was washed with deionized water and filled with 0.2 M NaOH. The solution was kept at −0.3 V vs. Hg/HgO reference electrode until the background current was reduced below 0.03 μA/cm². Then the cathodic compartment was filled with a supporting electrolyte containing 0.5 M HCl. The membrane was then saturated with hydrogen to fill possible irreversible trapping sites in the membrane by keeping the cathodic side applied potential of −0.8 V vs. SCE until the measured permeation current was constant. Prepared nitrogen was bubbled through both compartments to keep them free of dissolved oxygen. All experiments were carried out at constant volume, inhibitor concentration, temperature, pressure, and substrate surface area.

Results and Discussion

Permeation experiments were performed to clarify the role of organic inhibitors (PP and PN) on hydrogen entry kinetics in acidic media. To determine the hydrogen entry kinetics into C-1010 steel, experiments were carried out in 0.5 M HCl to measure the cathodic current density and the permeation current density as a function of the applied overpotential. In these experiments, the alloy membrane on the cathodic side of the cell was polarized potentiostatically. The hydrogen permeation transient into a bipolar membrane in a diffusion mode can be presented by the following equations obtained for two typical boundary conditions: (i) for the case where the hydrogen concentration at the entry side of the membrane is constant

\[ \frac{j_t}{j} = 1 + 2 \sum_{n=1}^{\infty} \left(-1\right)^n e^{-\frac{n^2 \pi^2 t}{L^2}} \]

and (ii) for the case where the flux of the hydrogen entering the membrane is constant

\[ \frac{j_t}{j} = 1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \left(-1\right)^n e^{-\frac{2n^2 \pi^2 t}{L^2}} \]

where \( j \) is the transient hydrogen permeation current density, \( j_s \) is the steady-state hydrogen permeation current density, \( j_i \) is the initial hydrogen current density, and \( \tau = tD/L^2 \), where \( t \) is time, \( L \) is the membrane thickness, and \( D \) is the hydrogen diffusivity.

Equations 1 and 2 are compared in Fig. 1 to our experimental permeation curve for a 1010 steel membrane (obtained in the absence of inhibitor in the electrolyte). As shown in Fig. 1 the experimental permeation curve is clos-
Fig. 3. The cathodic current inhibition efficiency of PN and PP vs. applied potential \( E \).

Fig. 4. Hydrogen permeation transients through a 1010 steel membrane at different applied potentials in the absence and presence of inhibitors. The membrane thickness is 0.03 cm.
permeation current inhibition efficiency increases up to 55%.

An attempt was made using the IPZ model to quantify the effect of the organic inhibitor on the hydrogen permeation process. The mechanistic model of Iyer et al. was used to determine the surface concentration and the hydrogen surface coverage, the hydrogen absorption, discharge, and recombination rate constants as well as HER coverage-dependent transfer coefficient, a, and the exchange current density, \( i_0 \), from a knowledge of the steady-state hydrogen permeation current, cathodic current, hydrogen diffusivity, and hydrogen overvoltage.

The IPZ model assumes that (i) the hydrogen reaction occurs via the coupled discharge-recombination mechanism, (ii) the recombination step of hydrogen is not rate-determining so that the hydrogen atom oxidation can be neglected, (iii) the Langmuir isotherm is used to describe the hydrogen coverage of the substrate, (iv) the intermediate hydrogen adsorption-absorption reaction is in local equilibrium, and (v) the hydrogen permeation process is described by a simple diffusion model through the membrane. With these assumptions one can derive the following relationships:

\[
i_\text{e} = i_0 (1 - \theta) e^{-\eta \text{F} / \text{RT}} \tag{3}
\]

\[
i = Fk_i \theta \tag{4}
\]

\[
e = \frac{k^n \theta}{b} \tag{5}
\]

\[
\eta = \frac{k^n \theta}{b} \sqrt{k_i} \tag{6}
\]

where \( i_\text{e} \) is the hydrogen recombination current density, \( i_0 \) is the exchange current density, \( b = \text{L/DF} \), \( \text{L} \) is the membrane thickness, \( F \) is the Faraday constant, \( D \) is the hydrogen diffusion coefficient, \( a = F/\text{RT} \), \( a \) is the transfer coefficient, \( \eta \) is the overpotential, \( R \) is the gas constant, \( T \) is temperature, and \( \theta \) is the hydrogen surface coverage, \( k_i \) is the recombination rate constant, \( i = i_0 (1 - \theta) \), where \( i_0 \) is the exchange current density, \( \theta \) is the equilibrium hydrogen coverage, and \( k^n \) is the thickness-dependent adsorption-absorption constant, defined as \( k_i \theta = k_i \theta m/L \) where \( k \theta m \) is the absorption rate constant for hydrogen into the metal and \( k_i \) is the desorption constant for hydrogen from the metal.

The dependence of the steady-state hydrogen permeation current upon the overpotential provided in this study is a diagnostic criterion for the identification of the mechanism of the discharge of hydrogen ions on the steel membrane. The experiments were carried out at a potential region where \( \eta >> \text{RT/F} \). In this region it was found that the slope of \(-d\eta/d \log (j) = 290 \text{ mV} \) (Theoretical value = 273 mV/decade = 2.3 \times 4RT/F \) (\( T = 298.15 \text{ K} \)) which indicates a coupled discharge-recombination mechanism, which is one of the assumptions for the applicability of the model.

Figures 7, 8, and 9 show the dependence of the steady-state permeation current upon the square root of the recombination current density in the absence of inhibitor and in the presence of 0.5 g/liter PN and 0.5 g/liter PP, respectively. The linear regression curves are shown as continuous lines in the figures and indicate that the permeation current inhibition efficiency increases up to 55%.
measurement rate is significantly lower when inhibitors were present in the electrolyte. The observed linear relationship of hydrogen permeation current upon the square root of the recombination current in the absence and presence of inhibitors is consistent with Eq. 6.

The permeation current densities, \( j_p \), vs. the charging function, \( i e^{\theta_m} \), in the absence and presence of PN are presented in Fig. 10. Figure 11 shows the same relationship but in the presence of PP in the electrolyte. Using the slopes and intercepts in Fig. 7 through 11 and Eq. 6 and 7, the values of \( i_{\infty}, k' \), and \( k_3 \) were calculated and are presented in Table I. Substituting the recombination constant, \( k_3 \), and the experimentally measured recombination current into Eq. 3, the hydrogen surface coverage was calculated and is presented in Fig. 12. The points were calculated from the IPZ model results at the experimentally tested overpotentials. As shown in Fig. 12, the hydrogen surface coverage decreases drastically in the presence of 0.5 g/liter of PP. The inhibitors cause a suppression of hydrogen surface coverage by adsorbing on the surface thus decreasing the substrate electroactive area for hydrogen discharge reaction. As a consequence, the hydrogen adsorption process is altered without changing the mechanical or physical properties of the substrate.

According to Eq. 5, the hydrogen permeation flux may be reduced by decreasing the hydrogen surface coverage by decreasing the absorption-adsorption constant. As shown in Table I, both the exchange current density and the adsorption-adsorption constant decrease in the presence of inhibitors. The decrease in the exchange current density accounts for the decrease in the cathodic current and consequently in a decrease of the hydrogen permeation current. PN reduces the hydrogen permeation rate by reducing the amount of hydrogen that discharges at the electrode surface, while PP reduces both the exchange current density and the adsorption-adsorption constant. Thus, the presence of PP in the electrolyte decreases the hydrogen discharge current and hydrogen permeation even at high cathodic potentials, up to 98 and 95%, respectively. The observed decrease of the hydrogen discharge and permeation currents in the presence of PP at high cathodic potentials indicates the potential for the use of PP in cathodic protection systems.

Our interpretation of the experimental data is that the model assumptions were reasonable in the potential region in which the inhibitors were studied. Despite the model limitations, we believe it is possible to compare the kinetic parameters in the presence and the absence of the inhibitors to quantify their effect.

It is important to point out that the values of the calculated model dependent parameters are valid as long as the assumptions of the IPZ model are applicable. This interpretation is also restricted to the potential area in which the parameters were estimated.

---

**Table I. IPZ model results.**

<table>
<thead>
<tr>
<th>Electrolyte/Parameter</th>
<th>( i_{\infty} ) (A cm(^{-2}))</th>
<th>( k' ) (mol cm(^{-3}))</th>
<th>( k_3 ) (mol cm(^{-2}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M HCl</td>
<td>7.3 x 10(^{-4})</td>
<td>7.02 x 10(^{-4})</td>
<td>1.07 x 10(^{-5})</td>
</tr>
<tr>
<td>0.5 M HCl + 0.5 g/liter PP</td>
<td>4.7 x 10(^{-4})</td>
<td>1.93 x 10(^{-4})</td>
<td>7.43 x 10(^{-3})</td>
</tr>
<tr>
<td>0.5 M HCl + 0.5 g/liter PN</td>
<td>1.6 x 10(^{-4})</td>
<td>3.51 x 10(^{-5})</td>
<td>2.79 x 10(^{-2})</td>
</tr>
</tbody>
</table>

---

Fig. 9. The steady-state hydrogen permeation current density, \( j_p \), obtained in the presence of 0.5 g/liter PP vs. the square root of the recombination current density, \( \sqrt{i_i} \).

Fig. 10. The steady-state hydrogen permeation current density, \( j_p \), vs. charging function, \( i e^{\theta_m} \), obtained in the absence of inhibitor and in the presence of 0.5 g/liter PN.

Fig. 11. The steady-state hydrogen permeation current density, \( j_p \), vs. charging function, \( i e^{\theta_m} \), obtained in the presence of 0.5 g/liter PP.

Fig. 12. The hydrogen surface coverage, \( \theta_h \), vs. applied potential, \( E \), estimated in the absence of inhibitor and in the presence of 0.5 g/liter PN and 0.5 g/liter PP.

---
Conclusions

The Devanathan-Stachurski permeation technique was used to determine the hydrogen entry kinetics through an iron membrane in the presence and absence of PN and PP inhibitors. Hydrogen evolution rates and hydrogen permeation rates were followed as a function of time at different applied potentials. The hydrogen discharge current at −0.6 V vs. SCE was reduced by 80 and 98% in the presence of PN and PP, respectively; hydrogen permeation current density was reduced by 55 and 95%, respectively. At −0.9 V vs. SCE in the presence of PN and PP in the electrolyte, the hydrogen permeation current inhibition was 35 and 95%, respectively and the discharge current density were reduced by 55 and 95%. It was found, according to the IPZ model, that PN reduces the hydrogen permeation rate by reducing the amount of hydrogen that discharges at the electrode surface, while PP reduces both, the exchange current density and the hydrogen adsorption-absorption constant.

Acknowledgment

Technical assistance and financial support by A. John Sedriks, the Office of Naval Research, under Contract No. AAESRT N00014-93-1-1094 are gratefully acknowledged.

Manuscript submitted July 30, 1996; revised manuscript received March 24, 1997.

The University of South Carolina assisted in meeting the publication costs of this article.

LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Greek</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>$F/RT$</td>
<td>a constant, V$^{-1}$</td>
</tr>
<tr>
<td>β</td>
<td>$L/(FD)$</td>
<td>a constant, (A cm)$^{-1}$</td>
</tr>
<tr>
<td>C$_{h}$</td>
<td>hydrogen surface concentration, mol cm$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>C$<em>{h}$$</em>{max}$</td>
<td>maximum hydrogen surface concentration, mol cm$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>hydrogen diffusivity, cm$^{2}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$E_c$</td>
<td>open-circuit potential, V</td>
<td></td>
</tr>
<tr>
<td>$E_0$</td>
<td>cathodic potential, V</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant, 96487 C/equivalent</td>
<td></td>
</tr>
<tr>
<td>$i_0$</td>
<td>current density, A/cm$^{2}$</td>
<td></td>
</tr>
<tr>
<td>$i_c$</td>
<td>cathodic current density, A/cm$^{2}$</td>
<td></td>
</tr>
<tr>
<td>$i_j$</td>
<td>hydrogen recombination current density, A/cm$^{2}$</td>
<td></td>
</tr>
<tr>
<td>$i_i$</td>
<td>exchange current density, A/cm$^{2}$</td>
<td></td>
</tr>
<tr>
<td>$i_d$</td>
<td>current density measured in the presence of inhibitor, A/cm$^{2}$</td>
<td></td>
</tr>
<tr>
<td>$i_d/(1 - \theta_d)$</td>
<td>A/cm$^{2}$</td>
<td></td>
</tr>
<tr>
<td>$j_a$</td>
<td>steady-state hydrogen permeation current density ($j_a = FDC_{h}D_0/1$, A/cm$^2$)</td>
<td></td>
</tr>
<tr>
<td>$j_i$</td>
<td>initial hydrogen permeation current density, A/cm$^{2}$</td>
<td></td>
</tr>
<tr>
<td>$j_t$</td>
<td>transition hydrogen permeation current density in the presence of inhibitor, A/cm$^{2}$</td>
<td></td>
</tr>
<tr>
<td>$t$</td>
<td>transition hydrogen permeation current density, A/cm$^{2}$</td>
<td></td>
</tr>
<tr>
<td>$k_r$</td>
<td>recombination rate constant, mol (cm$^2$ s$^{-1}$) $^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$k_d$</td>
<td>thickness dependence absorption-adsorption constant, mol cm$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>membrane thickness, cm</td>
<td></td>
</tr>
<tr>
<td>$P_i$</td>
<td>inhibitor efficiency $(1 - i)/i_j$, dimensionless</td>
<td></td>
</tr>
<tr>
<td>$P_i$</td>
<td>permeation current inhibitor efficiency $(i - j)/j_0$, dimensionless</td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant, 8.3143 J (mol K)$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>time, s</td>
<td></td>
</tr>
<tr>
<td>$t_1/2$</td>
<td>time corresponding to the half rise of the permeation curve, s</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>temperature, K</td>
<td></td>
</tr>
</tbody>
</table>

REFERENCES