EFFECT OF HYDROCARBON ON THE ACTION OF CO₂ CORROSION INHIBITORS

Ilim
Jurusan Kimia, FMIPA Universitas Lampung
Jl. Sumantri Brojonegoro No. 1 Bandarlampung, 35145, Indonesia

ABSTRACT

This research focused on a study of hydrocarbon effect on action of carbon dioxide corrosion inhibitors. Wheel test was used to determine the effectiveness of each inhibitor in the presence and absence of hydrocarbon at 50°C. The effects of hydrocarbon on the action of compounds used in this work gave different result on each compound. Oligomer of P4VP is chemisorbed on the mild steel surface shows that no significant effect of hydrocarbon. The corrosion rate of P2VP oligomer increases by adding hydrocarbon. Whole surfactants that were tested hydrocarbon effect show increasing corrosion rate in the presence of hydrocarbon due to the simple desorption of inhibitor from the surface.

Keywords: hydrocarbon effect, carbon dioxide corrosion inhibitors, wheel test

INTRODUCTION

Crude oils and petroleum-derived products vary significantly in their composition from one field to another. Generally, the crude oils phase contains aliphatic and aromatic hydrocarbons, heterocyclic and metal organic compounds, high molecular weight organic compounds, and a wide array of nitrogen, sulfur, and oxygen containing organic compounds\(^1\). Previous references stated that there is an empirical inverse relationship between the product of organic nitrogen content and the acid number for a crude oil with the corrosion rate\(^2\). This relationship provides an indication of the effects of crude oils on the corrosion rate of steel in a two-phase system. It is assumed that an oil phase will form a hydrophobic film over a steel surface protecting it from corrosive fluids. Factors such as interfacial properties of a crude oil can also influence the level of corrosion protection that is provided by oils.

Interfacial properties will determine whether the hydrocarbon phase will be transported to the metal surface. A hydrocarbon phase will generally decrease the corrosion rate\(^3\).

The hydrocarbons in crude oil interact with inhibitor films by forming another film on top of the pre-adsorbed inhibitor film. The secondary adsorption or co-adsorption of the hydrocarbon phase increases the hydrophobic character of the film. Production of this film (inhibitor and hydrocarbon) at the metal surface creates a more effective barrier against aqueous corrosive fluids.
MATERIALS AND METHODS

Materials

The corrosion electrolyte used was a brine solution. The brine solution was prepared by dissolving sodium chloride, NaCl, at 3% (w/v) and sodium bicarbonate, NaHCO₃, analytical reagent (AR), at 100 mg L⁻¹ in milli-Q water. The electrolyte was saturated with CO₂ at atmospheric pressure by purging the solution with CO₂ gas (FG) at a rate of approximately 150 – 200 mL min⁻¹. Kerosene was used as the hydrocarbon solution.

Corrosion inhibitor solutions were made by dissolving the inhibitor compounds in appropriate solvents, including ethanol, methanol, milli-Q water and sometimes a mixture of solvents. Stock solutions of the inhibitors were prepared between 1000 and 10,000 mg L⁻¹.

Preparation of Coupons

Coupons (2 x 1 x 0.1 cm) were prepared by sand blasting a sheet of mild steel with garnet (size 0.89 mm) and using a guillotine to cut it to size. The coupons were degreased by placing them in a beaker of ethanol and sonicating for two minutes. The coupons were dried and the dimensions and weights were accurately recorded.

Preparation of the Bottles

Clean, heavy duty, soda glass bottles (220 mL) were filled with 175 mL of fluid. The amount of brine solution (3% w/v AR sodium chloride and 100 mg L⁻¹ AR sodium bicarbonate) and/or kerosene added to bottles was determined by the kerosene/brine ratio being investigated. The appropriate inhibitor solution was pipetted into the bottles using a micro pipette and the mixture was sparged for 45 minutes with carbon dioxide gas (at about 250 mL min⁻¹). A steel coupon was placed in to each bottle and the sparging pipette was carefully removed to ensure that there was no oxygen contamination. The bottles were capped with crown seals and placed in a wheel oven at 50°C for 24 hours. All tests were done in either duplicate or triplicate.

Removal of Coupons

The bottles were removed from the oven and uncapped. The coupons were removed and immediately placed in Clarke's solution (an inhibited acid) for 45 seconds in order to remove the corrosion product from the surface. It was dipped into water (5 seconds) prior to an ethanol rinse (5 seconds) and then the coupons were dried and accurately weighed.

RESULTS AND DISCUSSION

Weight loss measurement using the wheel test was provided to determine the effect of hydrocarbon in the action of the carbon dioxide corrosion inhibitors. The wheel test used in this research project provided an integrated corrosion rate via the following Equation (1):

$$CR(\text{mmpy})=10\times(Wt/A)\times(1/D)\times(365/t)$$  (1)

where:  
CR = Corrosion rate (mmpy)  
Wt = Weight loss (gram)  
A = Area of coupon (cm²)  
D = Density of metal (g cm⁻³), equal to 7.86 g cm⁻³ for carbon Steel  
t = Time of exposure (days)

In weight loss, a metal coupon of known surface area is exposed to the environment and the corrosion rate is determined from the weight of metal lost during the exposure period. The period of exposure depends upon the corrosion rate and can be any period from 1 to 30 days, or more. The technique has the advantage of being able to detect localized forms of corrosion. It provides an integral measurement of corrosion.
rate during the period of exposure but has the disadvantage of not being able to detect sudden changes in corrosivity that may take place within the plant or process stream.\(^4\)

Previously, the thermodynamic parameters of adsorption for some pure corrosion inhibitors have been determined by Temkin adsorption isotherm\(^3,5\). The work indicated that some compounds were unequivocally chemisorbed at the steel surface, via their endothermic adsorption enthalpies. Others could not be assigned with certainty to either chemisorption or physisorption. The study of inhibitor adsorption was conducted in brine solution and used at a constant concentration of inhibitor, which is analogous to the process of continuous injection. Undoubtedly, the adsorption study is applicable to wet gas situations (i.e., the absence of a hydrocarbon phase), however the behavior of inhibitors in an oil well is also affected by the presence of multiple phase.

The corrosion rates in the presence and/or absence of hydrocarbon (kerosene) are shown in Table 1 and Figure 1.

In general, most of the compounds shown in Figure 1 reduce the CO\(_2\) corrosion rate in the absence of hydrocarbon, while the corrosion rates increase in the presence of the hydrocarbon. The interaction of hydrocarbon with some inhibitors has markedly improved the corrosion rates that mean that there is coadsorption on the process. The compounds with enthalpies of adsorption indicative of chemisorption (i.e, P4VPs) experienced no significant effects of the hydrocarbon. Other compounds with enthalpies of adsorption closer to that which is generally considered physisorption (i.e P2VP, appeared to experience an increase in corrosion rate in the presence of a hydrocarbon as a result of simple desorption of inhibitor from the surface.\(^5\) The similar results were also found by Durnie.\(^6\)

### Table 1. Corrosion rates of the CO\(_2\) corrosion inhibitors in presence and absence of the hydrocarbon phase

<table>
<thead>
<tr>
<th>Inhibitor Code</th>
<th>CR(mmpy) in No kerosene</th>
<th>CR(mmpy) in Kerosene</th>
<th>Inhibitor Code</th>
<th>CR(mmpy) in No kerosene</th>
<th>CR(mmpy) in Kerosene</th>
</tr>
</thead>
<tbody>
<tr>
<td>AI (5 ppm)</td>
<td>0.98</td>
<td>2.08</td>
<td>P2VPC (50 ppm)</td>
<td>1.71</td>
<td>1.98</td>
</tr>
<tr>
<td>CDS (2 ppm)</td>
<td>0.47</td>
<td>2.58</td>
<td>P4VPA (50 ppm)</td>
<td>1.08</td>
<td>1.13</td>
</tr>
<tr>
<td>CDT (50 ppm)</td>
<td>1.69</td>
<td>2.68</td>
<td>P4VPB (50 ppm)</td>
<td>1.09</td>
<td>1.07</td>
</tr>
<tr>
<td>CDZ (5 ppm)</td>
<td>1.08</td>
<td>1.49</td>
<td>P4VPC (50 ppm)</td>
<td>1.12</td>
<td>1.19</td>
</tr>
<tr>
<td>Crovol (25 ppm)</td>
<td>1.41</td>
<td>2.80</td>
<td>P4VPD1 (50 ppm)</td>
<td>1.66</td>
<td>1.82</td>
</tr>
<tr>
<td>DMT (1 ppm)</td>
<td>0.97</td>
<td>2.65</td>
<td>P4VPPB (10 ppm)</td>
<td>1.22</td>
<td>1.45</td>
</tr>
<tr>
<td>KMT (5 ppm)</td>
<td>1.66</td>
<td>3.38</td>
<td>PVP (25 ppm)</td>
<td>3.04</td>
<td>3.27</td>
</tr>
<tr>
<td>P2VPA (50 ppm)</td>
<td>1.84</td>
<td>2.53</td>
<td>SPD (5 ppm)</td>
<td>1.25</td>
<td>2.19</td>
</tr>
</tbody>
</table>

\(© 2005\) FMIPA Universitas Lampung 49
CONCLUSIONS

The effects of hydrocarbon on the action of compounds used in this research gave different result on each compound. Oligomer of P4VP is chemisorbed on the mild steel surface shows that no significant effect of hydrocarbon. The corrosion rate of P2VP oligomer, physisorption compound, a little bit increase by adding hydrocarbon. Whole surfactants that were tested hydrocarbon effect show increasing corrosion rate in the presence of hydrocarbon.

ACKNOWLEDGMENTS

I thank to my supervisors, Prof. Alan Jefferson, Roland De Marco and Brian Kinsella, Curtin University of Technology, Perth, Australia for their suggestions. Thanks also go to LPIU-DUE Project Universitas Lampung for financial support.

REFERENCES


