

Effect of Hydrophobic Interaction on Corrosion Inhibitor Efficiency

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ABSTRACT

Surfactants are well known as an active ingredient of corrosion inhibitors; however, the molecular structure and its content of commercial inhibitors are not disclosed to users. The performance of commercial inhibitors was studied by treating the whole aspect of inhibitor as a kind of surfactant. The corrosion rate was measured with an autoclave by using an electrochemical measurement; namely, linear polarization resistance (LPR) in an oil flowline condition solution. Firstly, the corrosion rate was measured only with a corrosion inhibitor, and a hydrocarbon solvent was added afterwards. The decrease of the corrosion rate was observed after an addition of the solvent. Aliphatic, alicyclic and aromatic solvents with different octanol-water partition coefficients, K_{OW} , were tested in the same manner. The inhibitor efficiency was saturated remarkably after the addition of a solvent with high K_{OW} . The synergistic effect with a specific solvent in this test can characterize the hydrophobicity and the adsorption tendency of the commercial inhibitor without close chemical analysis to specify the surfactant in it.

Key words: Corrosion Inhibitor, CO₂ Corrosion, Hydrophobic Interaction, Surfactant

INTRODUCTION

Corrosion inhibitors are used to prevent pipeline corrosion in oil and gas industry. The evaluation of corrosion inhibitors is one of the most important tasks for the corrosion engineers. Corrosion of the metal is suppressed by the inhibitor adsorption on the metal surface. Active ingredients of corrosion inhibitors are, in general, surfactants. A surfactant can adsorb on the internal metal surface of piping and makes a hydrophobic film preventing the contact of water with the metal surface. Most corrosion inhibitors consist of organic solvents and organic compounds. The inhibitor efficiency can be determined by corrosion tests such as weight loss measurements and/or electrochemical techniques under simulated conditions. The recommendation and its feedback on a corrosion inhibitor are exchanged between a laboratory and a field, consequently the experience is acquired for the individual field in a general practice.

The majority of commercial inhibitors are specifically formulated for a particular application by its supplier. The inhibitor performance is highly dependent on the individual components within the formulation. However, the components are not always disclosed to the users except for Safety Data Sheet (SDS) data. In this study, a commercial corrosion inhibitor is treated as a single surfactant solution and the evaluation method was explored to interpret its adsorption mechanism. The mechanistic understanding of the corrosion inhibitor behavior in an aqueous solution will enhance the confidence and certainty of the corrosion inhibitor selection and its field application program.

X. Ko et al. studied the role of coadsorption of oil in corrosion inhibitor with molecular simulations.¹ Their results showed that oil molecules have a tendency to be co-adsorbed in the inhibitor films due to hydrophobic interactions and to form tightly packed films. The coadsorption effect depended on the kind of oil molecule in our previous experiment.² An objective of this study is also to verify those results experimentally.

EXPERIMENTAL PROCEDURE

Corrosion Test

The corrosion inhibitor performance at elevated temperature was evaluated with linear polarization resistance (LPR) in an autoclave. The electrode, i.e., the test coupon, is cut into 6 mm D x 20 mm L from C-steel pipe (ASTM^a A135³ Gr. A) The autoclave was filled with 1.8 L deionized water with 3,000 ppm chloride ions and 300 ppm acetic acid. After the solution was deaerated with CO₂ gas, it was pressured up to 0.3 MPa CO₂ gas at room temperature. When the autoclave reached the test temperature, 70 °C, the pressure reached approximately 0.8 MPa. Corrosion inhibitors and other additional chemicals were injected into the autoclave through a pump. The test solution was stirred gently with the stirrer rotating at 350 rpm during the corrosion test as shown in Figure 1. The wall shear stress on the test coupon is negligible. The LPR measurement is carried out every 5 minutes with PETROLITE M-3010^b to monitor the corrosion rate change during the corrosion test.

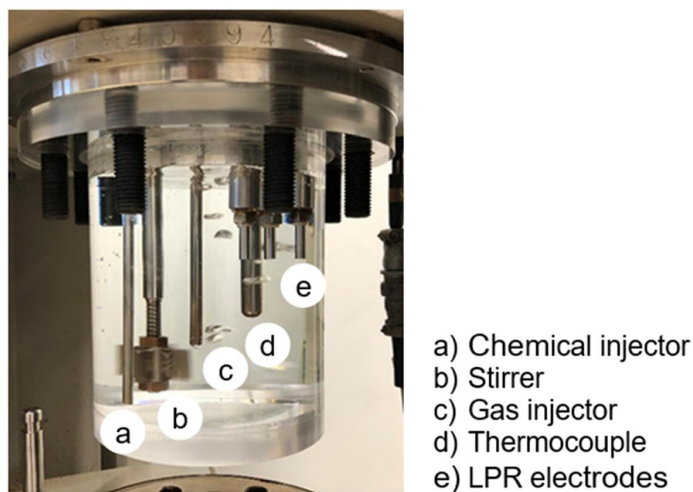


Figure 1: Autoclave with LPR electrodes

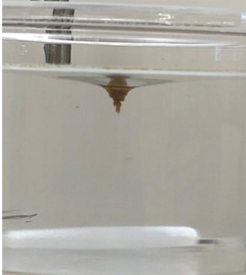
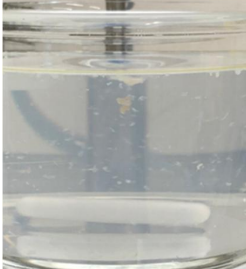
^a ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA, 19428-2959 USA

^b Trade name

Corrosion Inhibitor

Two commercial corrosion inhibitors, A and B, were examined. Their appearance, miscibility in water and experience in a gas condensate field are shown in Table 1. The value of "Ostensible" Hydrophilic-Lipophilic Balance (HLB) was solely estimated referring to Griffin's classification without molecule calculation.

Table 1
Corrosion inhibitor appearance and field experience

Inhibitor	Appearance *1	Miscibility in Water *2	Experience ⁴
A			More than 5 years for a flowline service under sweet corrosion condition. Available for a tubing batch treatment with heavy oil dilution. ← HLB 3-6 [Poor] *3
B			One year for a flowline service under sweet corrosion condition with lower dosage than A. Available for a high flow rate more than 4 m/s. ← HLB 6-8 [Milky dispersion with agitation] *3

*1 5 droplets in 60 mm evaporation dish

*2 Stirred in water at 150 rpm with 5 cm PTFE magnetic stir bar

*3 "Ostensible HLB" scale after Griffin's classification⁵

Hydrocarbon Solvent

Figure 2 shows examples of chemical compositions of a crude oil and a condensate oil. The crude oil includes more fraction of heavy ingredients than the condensate. The condensate oil includes more fraction of aromatic ingredients than the crude oil. Red circle markers in the figure (●) shows pure hydrocarbon solvents investigated in this study. Those hydrocarbon solvents were supplied as reagent grade. Figure 3 shows the physical properties of the hydrocarbon solvents and the molecular structures. K_{OW} serves as a measure of the relationship between hydrophobicity (oil solubility) and hydrophilicity (water solubility) of a substance. Aniline point is defined as the minimum temperature at which equal volumes of aniline and an oil are forming a single phase upon mixing. It indicates a detergency or a solubility of oil in nature. Unlike physical properties for the pure substance, the aniline point can be measured even for mixed oil. That is why aniline points are mentioned to compare solvents with each other in Figure 3. The aromatic solvent in the figure is a model oil, T-Sol 100[°] used in this study. The physical properties of the four pure solvents can cover those of crude, condensate and model oils.

[°] Trade name

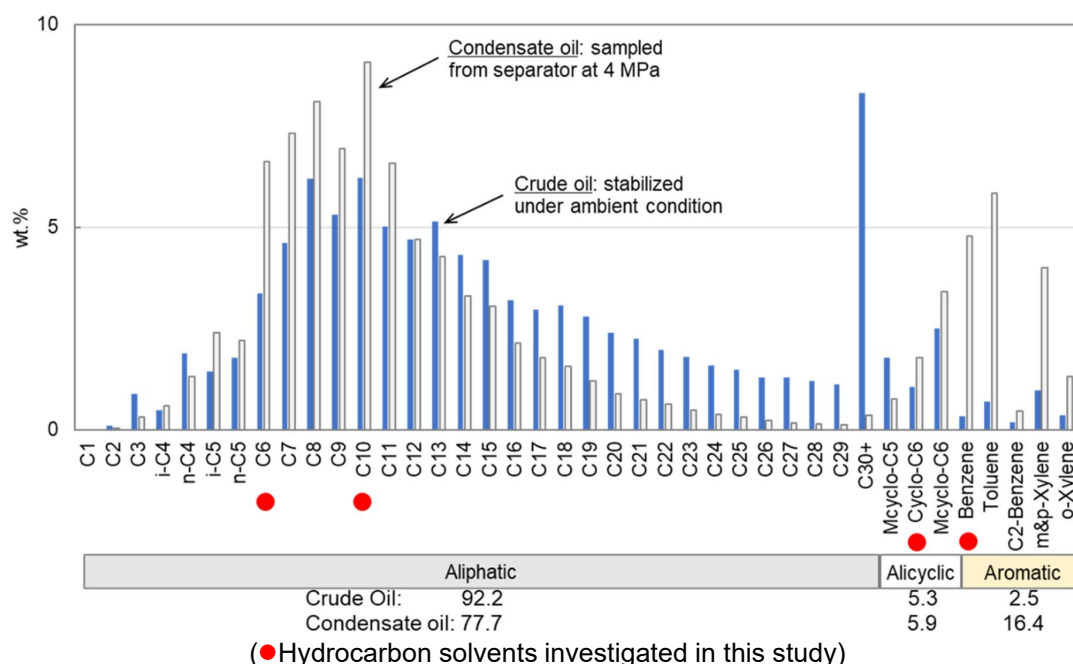


Figure 2: Chemical composition example of crude oil and condensate oil

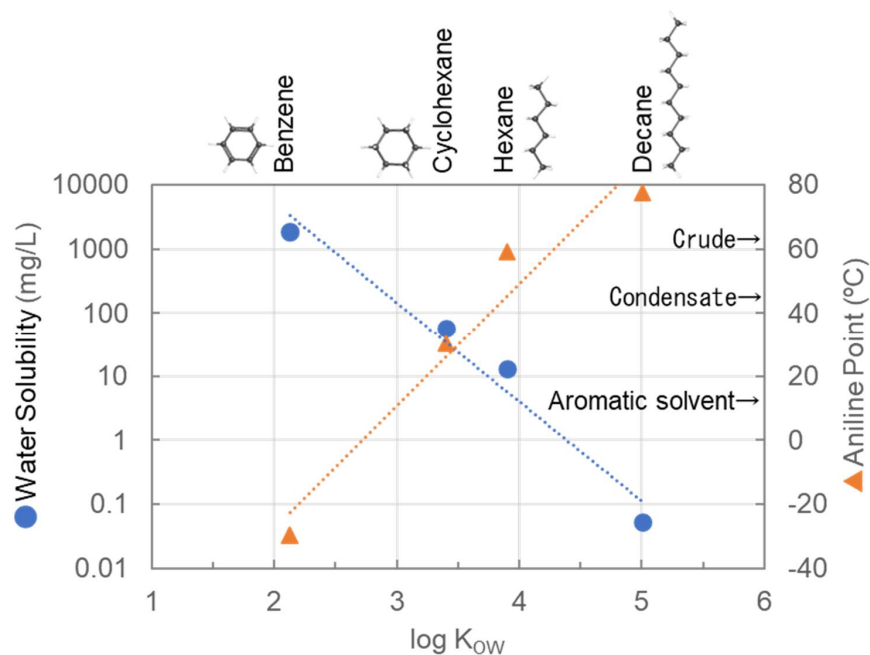


Figure 3: Physical properties of hydrocarbon investigated in this study

The miscibility of the inhibitors in the hydrocarbon solvents was examined before the corrosion test. A centrifuge tube containing 1 mL of inhibitor and 9 mL of hydrocarbon solvent was shaken intensely for one minute at the room temperature. The miscibility was observed until 2 h in a standing posture as shown in Figure 4. Some residual was recognized in hexane and decane which have higher K_{ow} .