

Micellization and Inhibition Efficiency

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ABSTRACT

Long-distance transmission of oil is usually carried out in large-diameter steel pipelines; water present therein may cause severe internal corrosion. An effective method of mitigating such corrosion is to inject organic corrosion inhibitors (CIs). Their surface adsorption, *via* heteroatom functionalities, can markedly enhance the corrosion resistance of metals. In this study, three CI model compounds with the same alkyl tail length ($-C_{14}H_{29}$), specifically benzyl-dimethyl-tetradecyl-ammonium (BDTA), tetradecyltetrahydropyrimidinium (TTHP) and tetradecylphosphate ester (TPE) were synthesized, their purities being determined using nuclear magnetic resonance spectroscopy (NMR). The critical micelle concentrations (CMCs) of each compound were measured using surface tensiometry (Du Noüy ring) and fluorescence spectroscopy techniques, and differences were found between these indirect and direct methods. In addition, linear polarization resistance was used to determine inhibition efficiencies (IEs) for carbon steel immersed in a NaCl electrolyte saturated with CO_2 . CI surface saturation concentrations, with maximum IEs, were compared with the determined CMCs. Excellent IEs were observed at concentrations of TTHP and TPE significantly less than their CMCs. These results imply that there is no direct link between CMC and corrosion efficiency and that the selection of the appropriate CI

concentration for an industrial application should not be based solely on CMC. Further work is ongoing to confirm this absence of correlation at higher temperature ($T > 30^{\circ}\text{C}$) and different water chemistry.

Keywords: corrosion inhibitors, critical micelle concentrations, inhibition efficiency, surface saturation concentration

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 reduce electrochemical reaction rates at the water-metal interface², 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 derivatives³. 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. Such molecules have a strong tendency to adsorb onto the steel surface and form self-assembled structures^{4, 5}. Surfactant-type organic inhibitors are, in some cases, applied based on their critical micelle concentration (CMC) values. However, recent work indicate that using CMC values as a measurement for injection of inhibitors might not be considered as a reliable factor⁶. CMC is an important characteristic of a surfactant. It is defined as the concentration of surfactants above which micelles form and all additional surfactant molecules added to the system aggregate as micelles⁷. As shown in Figure 1, below the CMC, the surfactant molecules will partition between the volume of the liquid and the gas-liquid interface with some CI molecules dispersed in the aqueous phase. Above the CMC, the concentration at the gas-liquid interface will not change anymore: any added surfactant molecule will tend to participate in the formation of micelles.

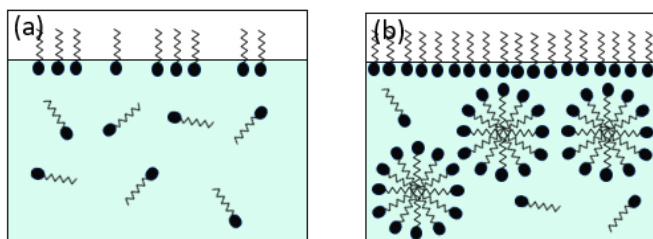


Figure 1: Scenarios for different concentrations of the inhibitor in solution: (a) Below CMC; (b) Above CMC

According to previous studies^{8–10}, when the metal exhibits a maximum reduction of corrosion rate, its surface is considered to have reached a state of maximum coverage by inhibitor molecules; increasing the concentration of inhibitor in solution would not lead to an increase in surface coverage and the inhibited corrosion rate would remain constant. Hypothetically, this scenario can be said to also correspond to a situation where the inhibitor concentration reaches CMC, the inhibitor molecules cannot

continue to accumulate at interfaces and instead start forming micelles. Coincidentally, it is common to observe a sharp decrease in corrosion rate with the addition of CI but only to a certain concentration, above which no change in IE can be noticed. This threshold concentration, labeled surface saturation concentration and corresponding to a condition of maximum IE¹¹ have been often associated with CMC. Consequently, CMC has been used as an important parameter in determining corrosion inhibitor application concentrations and efficiencies. However, recent studies within our laboratory indicate that there is no direct link between CMC and surface coverage, and by extension corrosion inhibition efficiency⁶.

This paper reports the synthesis of three CI model compounds with the same alkyl tail length (-C₁₄H₂₉), namely benzyldimethyltetradecylammonium (BDTA), tetradecyltetrahydropyrimidinium (TTHP) and tetradecylphosphate ester (TPE), their purities being determined using nuclear magnetic resonance spectroscopy (NMR). The critical micelle concentrations (CMCs) of each compound were measured at 25°C using surface tensiometry (Du Noüy ring) and fluorescence spectroscopy (FS) techniques. Linear polarization resistance (LPR) was used to determine inhibition efficiencies (IEs) for carbon steel immersed in a NaCl electrolyte saturated with CO₂. CI surface saturation concentrations, with maximum IE, were compared with the determined CMCs.

EXPERIMENTAL METHODOLOGY

Synthesis of Corrosion Inhibitor Model Compounds

Synthesis of benzyldimethyltetradecylammonium (BDTA)

The synthesis reaction for benzyldimethyltetradecylammonium (BDTA) bromide is as depicted in Figure 2. In this synthesis, acetonitrile (CH₃CN) was chosen as the solvent as it was reported to achieve high amine quaternization rates^{12, 13}.

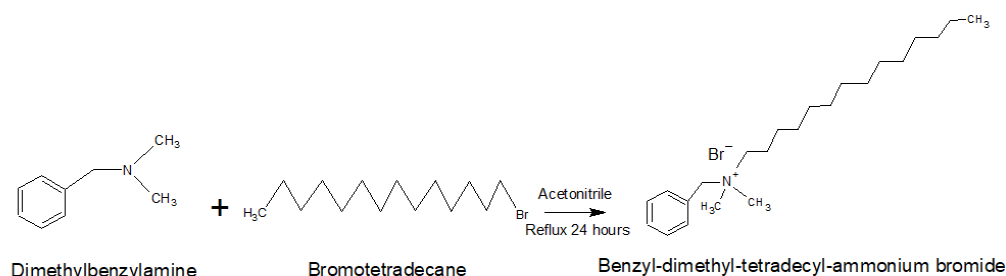


Figure 2: The reaction for the model compounds BDTA utilized as a corrosion inhibitor

The following presents the general procedure used for synthesizing the corrosion inhibitor model compound BDTA:

- (a) 13.52g (0.100 moles) of dimethylbenzylamine is added directly into a 2-necked 250mL round-bottomed flask (24/29 joints).
- (b) Acetonitrile solvent (100 mL) is then added, along with a few boiling chips.

- (c) A condenser and an addition funnel containing 27.73 g 1-bromotetradecane (also equivalent to 0.100 moles) are placed in each joint.
- (d) The round-bottom flask is then heated to the reflux temperature (82 °C) by an appropriately sized heating mantle connected to a Variac.
- (e) A flow of water runs through the condenser to ensure the reaction mixture (acetonitrile/amine mixture) is heated to the reflux temperature of ca. 82 °C.
- (f) The 1-bromotetradecane is then added dropwise from the addition funnel.
- (g) Reflux is maintained for a further 24 hours, then the reaction mixture is cooled to room temperature.
- (h) After the quaternization reaction is completed, the solvent is removed from the system by rotary evaporation.

Synthesis of 1-tetradecyl-1,4,5,6-tetrahydropyrimidinium (TTHP)

The synthesis reaction is as depicted in Figure 3. In this reaction, a hydrogen ion (H^+) resides on the more basic N atom; the N involved in the double bond. This N is more basic because a more stable (resonance stabilized) cation forms after protonation. However, it does not matter which of the two N's in 1,4,5,6-tetrahydropyrimidine is alkylated. In both cases, the same product forms. The final product is the one in which the positive charge is delocalized between the two nitrogen atoms. The real structure (resonance hybrid) is somewhere between the structures of the two resonance structures drawn in the below reaction scheme.

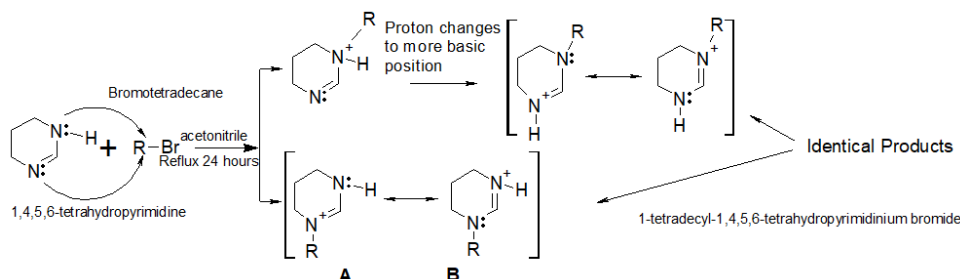


Figure 3: The reaction for the synthesis of the TTHP model compound.

The following is the procedure for the synthesis of 1-tetradecyl-1,4,5,6-tetrahydropyrimidinium, this is the same as that used in the synthesis of BDTA with tetrahydropyrimidine replacing dimethylbenzylamine:

- (i) 4.85 g (0.0576 moles) of 1,4,5,6-tetrahydropyrimidine is weighed directly into a 2-necked 250mL round-bottomed flask (24/29 joints).
- (j) Acetonitrile (100 mL) is added.
- (k) The round-bottom flask is placed in an appropriately sized heating mantle, four boiling stones being put into the flask to make sure there are plenty of nucleation sites for bubbles to form and prevent reaction mixture “bumping”.
- (l) The condenser and addition funnel containing 15.98 g (0.0576 moles) of 1-bromotetradecane are placed in each joint.

- (m) Cooling water is run through the condenser. The heating mantle, connected to a Variac, is switched on and set to ensure the reaction mixture (acetonitrile/pyrimidine mixture) is heated to the reflux temperature of ca. 82 °C.
- (n) The 1-bromotetradecane is then added dropwise to the reaction mixture, as shown in Figure 4 (a).
- (o) Reflux is maintained for a further 24 hours then the reaction mixture is cooled to room temperature.
- (p) The acetonitrile is removed by rotary evaporation (Figure 4 (b)). The temperature is increased to 95 °C, under vacuum, to drive off any residual volatile species.

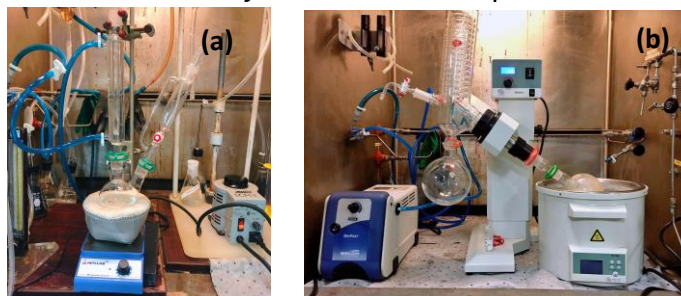


Figure 4: (a) Reflux system for amine alkylation. (b) Recovery of products by rotary evaporation.

Synthesis of Tetradecyl Phosphate Ester (TPE)

- *First step: Esterification*

The purpose of this step is to obtain a crude product, which may contain monoester, diester, H_3PO_4 , and inorganic phosphates. The reaction is shown in Figure 5, where ROH is 1-tetradecanol ($\text{C}_{14}\text{H}_{29}\text{OH}$). Note the reaction has no solvent.

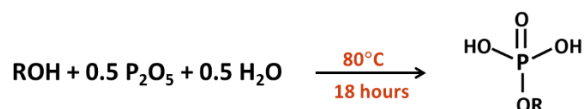


Figure 5: Reaction for esterification

- *Second step: Liquid-liquid extraction.*

The purpose of this step is to remove H_3PO_4 and inorganic phosphates.

- *Third step: Rotary evaporation.*

The purpose of this step is to remove diethyl ether introduced by the second step as a solvent.

The following are the procedures for the synthesis of tetradecyl phosphate ester.

- *First step: Esterification.*

- a) 42.8 g (0.2 moles) of solid 1-tetradecanol is weighed directly into a 3-necked 250mL round-bottomed flask.
- b) 14.1g (0.1 moles) phosphorus pentoxide is added and mixed with the 1-tetradecanol.
- c) Flask is set in a heating mantle.
- d) Condenser, thermometer and addition funnel are placed in each joint.