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Integrated evaluation of mixed surfactant distribution in water-oil-steel pipe environments and associated corrosion inhibition efficiency

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ABSTRACT

One multiphysics model, integrated corrosion inhibition (ICI) model, has been theoretically introduced and experimentally validated for the integrated evaluation of water-oil partitioning, aggregation, adsorption/desorption, and corrosion inhibition of mixed surfactant inhibitors in salt-containing water-oil-steel pipe (WOS) environments. The ICI model is based on three major sub-models which consider water-oil surfactant partitioning, micellization, effective adsorption/desorption on substrate, surfactant type, surfactant-solvent interactions, surfactant-counterion pair, and lateral surfactant interactions etc., and intended to serve as a basic framework in the design, selection, optimization, and utilization of various pure and mixed surfactant inhibitors in WOS environments.

1. Introduction

Carbon steel is one of the most widely used metals in production and transportation in the oil and gas industries [1–3]. However, carbon steel is highly susceptible to corrosion in environments that contain water, CO_2, H_2S, and various ions (such as Cl^-), etc. [4,5]. The presence of CO_2 in oil pipelines exposes carbon steel components to substantial damage due to the accelerated corrosion, which eventually threatens environments, production, and safety [4,6,7]. An illustrated example of a corroded sample, a piece of X65 steel, which is commonly used in oil pipelines, is shown in Fig. 1(a).

A variety of methods for CO_2-related corrosion control have been developed. The use of surfactant inhibitors has received extensive attention in the oil and gas industry for corrosion inhibition of production and transportation pipes (metallic materials, such as steel and copper) in a way that surfactant molecules usually adsorb on steel surface and form a protective film which acts as a barrier to reduce corrosive media penetration and attack [1–4,8,9]. Inhibitor mixtures have been used in wide ranging applications due to their superior physicochemical properties and capabilities in efficient solubilization, adsorption, and transportation [4,10,11]. Inhibitor mixtures can often be conveniently tuned to achieve desired properties by adjusting surfactant type and mixture ratios [12]. More surface-active and expensive inhibitors are often mixed with less surface-active and cheaper inhibitors to reduce cost [4,5]. Many of the organic inhibitors, are surfactant molecules with hydrophilic and hydrophobic molecular sections, which increases the complexity of their interactions in water-oil-steel pipe (WOS) environments.

The hydrophilic portion of surfactant strongly favors interactions with polar entities such as water, metals, and ions, which facilitates surfactant aggregation and surfactant adsorption on metal surfaces, blocks active surface sites, and thereby protects metal from corrosion [8,9]. On the other hand, surfactant molecules tend to escape from polar aqueous phase by associating and aggregating hydrocarbon chains together because of hydrophobicity [9,13].

When an aqueous solution containing surfactant comes into contact with an immiscible organic liquid in one environment, such as water-oil interface, surfactant monomers with longer hydrocarbon chains prefer partitioning into the organic liquid until equilibrium is reached [14–19], which usually reduces the availability of surfactant monomers in the aqueous phase for adsorption on the metal surface and for corrosion inhibition. The partitioning is usually characterized by the partitioning coefficient, which

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Nomenclature

List of symbols

A_e	Electron affinity
$\vec{A}$	A vector of regression coefficients specific to surfactant/mixture and solution conditions
$\vec{A}'$	A modified vector of regression coefficients
$\bar{B}$	A regression constant
$\bar{B}'$	A modified regression constant
C_c	The concentration of counterion dissociated from electrolyte salt and from ionic surfactant in aqueous solution
C_m	The average concentration of total monomeric surfactant in WOS environments
C_{mo}	The mole concentration of oil
C_{mw}	The mole concentration of water
C_{tol}	The initial concentration (not at equilibrium) of total surfactant added to aqueous phase
C_m^o	The concentration of total monomeric surfactant in oil phase
C_{mi}^o	The concentration of monomeric surfactant 'i' in oil phase
C_m^w	The concentration of total monomeric surfactant in aqueous phase
C_{mi}^w	The concentration of monomeric surfactant 'i' in aqueous phase
$\bar{C}$	The overall average concentration of total surfactant in water and oil phases
E_{corr}	Open circuit potential
E_{HOMO}	Energy of highest occupied molecular orbital
E_{ip}	Ionization potential
E_{HOMO}	Energy of lowest unoccupied molecular orbital
f_i	Activity coefficient of surfactant 'i' in micelles
i	Arbitrary surfactant
i_a	Anodic current density
i_c	Cathodic current density
i_{corr}	Corrosion current density with surfactant inhibitors in solution
i_{meas}	Measured current density
i_{ocorr}	Corrosion current density without surfactant inhibitors in solution
j	Arbitrary counterion
K_{ad}	Equilibrium adsorption constant
K_i	The partitioning coefficient of pure surfactant 'i'
K_{mix}	The apparent partitioning coefficient of surfactant mixture
K'	A constant equal to the equilibrium adsorption constant K_{ad} multiplied by Γ^w
M_{ad}	The surfactant adsorbed on steel surface and water/oil interface
M_o	The surfactant (both monomeric and micellar forms) distributed in the oil phase
M_{tol}	The total quantity of surfactant added to the WOS environments
M_w	The surfactant (both monomeric and micellar forms) distributed in the water phase
$\vec{Q}$	A vector of quantum chemical descriptors for a particular surfactant or surfactant mixture
R	Gas constant
R_p	Polarization resistance in the presence of surfactant
R_{po}	Polarization resistance in the absence of surfactant
T	Temperature
V_o	Volume of oil phase
V_w	Volume of water/aqueous phase
x_i	The mole fraction of surfactant 'i' in total surfactant mixture in bulk solution
X_{mi}^o	The mole fraction of surfactant 'i' in total amount of molecules in oil phase
X_{mi}^w	The mole fraction of surfactant 'i' in total amount of molecules in oil phase
X_j^w	The mole fraction of counter 'j' in total amount of molecules in water phase
αi	The mole fraction of surfactant 'i' in mixed micelles at partitioning and adsorption equilibrium
α_i'	The mole fraction of surfactant 'i' in mixed micelles without partitioning process
β_a	Anodic tafel slope
β_c	Cathodic tafel slope
γ_c	The mean activity coefficient of counterion
γ_{mi}^o	Activity coefficient of monomeric surfactant 'i' in oil phase
γ_{mi}^w	Activity coefficient of monomeric surfactant 'i' in water phase
γ_{mj}^w	Activity coefficient of counterion 'j' in water phase
Γ_{app}	The apparent cmc of surfactant mixture which is defined as the average concentration of mixed surfactants at which mixed micelles start to form in WOS environments
$\Gamma_{app,i}$	The apparent cmc of surfactant 'i' which is defined as the concentration of surfactant at which micelle starts to form in WOS environments
Γ_i^o	The cmc value of surfactant 'i' in oil phase
Γ_i^p	The cmc of surfactant 'i' in pure water
Γ^w	The cmc value of surfactant mixture in aqueous phase
Γ_i^w	The cmc value of surfactant 'i' in aqueous phase
δ_i	An experimental constant that is interpreted as the counterion binding coefficient with respect to surfactant 'i'
δ_j	The binding coefficient to micelles with respect to counterion 'j'
ΔE	Energy difference between HOMO and LUMO
ΔN	The fraction of electrons transferred from the surfactant to the steel surface
$\Delta\mu_{tri}^o$	The standard free energy change of surfactant 'i' transferring from water to oil
Υ	Global hardness
Υ_{inh}	Global hardness of surfactant molecule
Υ_{mel}	Global hardness of metals (electrodes)
$\eta(\%)$	Corrosion inhibition efficiency
θ	The effective surface coverage and assumed to be equal to corrosion inhibition
μ_i^m	The chemical potential of surfactant 'i' in mixed micelles
μ_i^o	The chemical potential of monomeric surfactant 'i' in oil phase
$\mu_i^{o,o}$	The standard chemical potential of monomeric surfactant 'i' in oil/organic phase
μ_i^{pm}	The chemical potential of surfactant 'i' in pure micelles
μ_i^w	The chemical potential of monomeric surfactant 'i' in water phase
$\mu_i^{w,o}$	The standard chemical potential of monomeric surfactant 'i' in water/aqueous phase
μ_j^w	The chemical potential of counterion 'j' in water phase