Experimental Investigation and Modeling of the Performance of Pure and Mixed Surfactant Inhibitors: Aggregation, Adsorption, and Corrosion Inhibition on Steel Pipe in Aqueous Phase

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Two models for the prediction of corrosion inhibition efficiency of various pure surfactant and mixed surfactants in salt-containing solution are developed, compared, and validated. The two prediction models are based on a modified Langmuir adsorption (MLA) sub-model and a modified Quantitative Structure Activity Relation (MQSAR) sub-model. Each of the sub-models is combined with the critical micelle concentration (cmc) prediction sub-model to create an overall corrosion inhibition prediction model separately. Each of the created overall models is very robust in predicting corrosion inhibition of various surfactants in a variety of testing systems. The model derivation is mainly based on the mixed homologous benzalkonium chlorides in NaCl-containing aqueous solution and further validated using various testing systems of surfactants. The developed corrosion inhibition prediction models provide potential methods to evaluate the effectiveness of various surfactants in corrosion inhibition under various testing solution conditions. In addition, the adsorption and inhibition mechanisms of surfactants in the corresponding testing system were investigated.

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Carbon steel is widely used for production and transportation pipelines in the oil and gas industries.14,17 However, carbon steel is easily corroded in environments that contain water and carbon dioxide (CO2).2,3,4 As one of the main corrosion types in the oil and gas industry, CO2-related corrosion can cause tremendous damage to pipelines and structural components in water and crude oil transportation and thus threaten production and safety.3,5,7,8 The annual direct cost of corrosion in United States has been estimated to be around 3.1% of the gross domestic product (GDP). About 3.7% out of the total cost comes from the oil and gas industry,10 which is mainly due to the corrosion of carbon steel. Therefore, the cost of corrosion and safety has led to great interest in controlling CO2-related corrosion in various oilfields around the world.

The most popular control method is to use organic inhibitors that contain hydrophobic molecules to reduce CO2 based corrosion on carbon steel.12,11–14 Many of the organic inhibitors are surfactants with hydrophilic and hydrophobic molecular sections.

The hydrophilic group of surfactant strongly prefers interaction with polar entities such as water, metals, and ions. These organic surfactants adsorb on the metal surface, block the active surface sites, and thereby reduce corrosion attack.3,11 The presence and structure of specific atoms, such as N and O, in surfactants determine the adsorption mechanism and corrosion inhibition efficiency.13,14 Surfactant mixtures have received wide attention in practical applications because of their superior physicochemical properties and capabilities in efficient solubilization, dispersion, suspension, and transportation.15,16 Solutions containing mixed surfactants can often be conveniently tuned to achieve desired properties by adjusting the composition of the mixture. More surface-active and expensive surfactants are usually mixed with less surface-active and less expensive surfactants to reduce cost.17 However, the authors are not aware of a completely established theory or model to adequately predict corrosion inhibition using mixed surfactants despite extensive research work3,18–24.

Because of hydrophobicity, surfactant molecules tend to adsorb at the air-liquid interface, liquid-solid interface, or liquid-liquid interface to escape from the aqueous phase by associating and aggregating hydrocarbon chains together.15–17 The concentration at which a monolayer covers the solid-liquid interface is considered as the surface aggregation concentration (sac). Above the sac, surfactants will form aggregate structures to orient their hydrophobic tails toward those of neighboring surfactant molecules and their hydrophilic head groups toward water. The concentration at which surfactants start to form aggregates in solution is termed the critical micelles concentration (cmc).21–23

It is often assumed that the corrosion rate in the presence of low concentration of surfactants (usually lower than sac) can be represented by the number of available surface sites remaining after limited surfactant adsorption.21–23 As the concentration of surfactants increases, more and more active surface sites are covered by surfactants. Near the sac or cmc, the metal surface is assumed to be nearly covered by one monolayer or multilayers of surfactants, respectively, and metal is well protected from corrosion attack.21–23 Thus, sac and cmc are important factors in the evaluation of the effect of surfactant concentration on surfactant adsorption and corrosion inhibition of metal. However, there is a lack of investigation and associated modeling work that illustrate how sac and cmc affect corrosion inhibition efficiency of surfactants in solutions with various dissolved salt contents.

In the present study, a new model for prediction of corrosion inhibition efficiency in salt solution using surfactants (both pure and mixture) is introduced based on previous work.21–25,27 This model is based on utilization of either a Langmuir adsorption (LA) sub-model or a Quantitative Structure Activity Relation (QSAR) sub-model with a cmc prediction sub-model.27 The developed model is referred to as a modified Langmuir adsorption (MLA)25 or modified Quantitative Structure Activity Relation (MQSAR) model, respectively, and will be introduced in the following section. The predictive MLA and MQSAR models are validated using electrochemical data collected from X65 steel corrosion inhibition testing using mixed homologous benzalkonium chlorides (BAC) surfactants as well as the reported data on other testing systems (Table 1). The chemical structure of various surfactant molecules discussed in the present work is given in Fig. 1. The predicted results from MLA and MQSAR agree well with experimental results. In addition, the effect of BAC concentration on steel corrosion inhibition as well as the associated adsorption mechanism on steel is discussed based on electrochemical measurements and density functional theory (DFT) calculations.

Model Derivation

MLA sub-model.— One of the widely accepted models which is used for the adsorption of surfactants at an electrode-solution interface is the Langmuir adsorption model,21–25,30 in which the surface...
where \( \theta \) is the equilibrium adsorption constant given by

\[
\theta = \frac{1}{K_{ad} C} + 1
\]  

where \( K_{ad} \) is the equilibrium adsorption constant given by

\[
K_{ad} = \frac{1}{C_{wm}} \exp \left( -\frac{\Delta G^o}{RT} \right)
\]

where \( C \) is the concentration of surfactant in the bulk solution, \( C_{wm} \) is the molar concentration of water which is 55.5 M, \( \Delta G^o \) is the standard free energy of adsorption, \( R \) is gas constant, and \( T \) is absolute temperature.

As mentioned in the former section, sac (represented using \( \Gamma \)) and cmc (represented using \( \Gamma \)) are important parameters characterizing corrosion inhibition efficiency of surfactants. Therefore, MLA is introduced to evaluate corrosion inhibition efficiency of surfactants under various solution conditions by the incorporation of the cmc considering that the cmc is easier to measure and predict than sac.\(^\text{25}\) The MLA is presented below

\[
\frac{1}{1 - \theta} = 1 + K' C
\]

or

\[
\eta(\%) = 1000 \left( 1 - \frac{1}{1 + K' C} \right) \times 100
\]

where \( K' \) is equal to the adsorption constant \( K_{ad} \) multiplied by \( \Gamma \), and \( \eta \) is corrosion inhibition efficiency. Note homologous surfactants tend to achieve similar levels of surface coverage at similar ratios of surfactant concentration to surfactant cmc, so the value of \( K' \) barely varies for homologous surfactants and can be used as a universal constant for such homologous surfactants.\(^\text{25}\) Note that \( C \) can increase above the sac or the cmc, but the fitting will not be as good as the fitting for \( C \) below the sac as shown in the following sections, which show that the sac is a transition point in characterizing the effectiveness of surfactants as corrosion inhibitors. The essence of Eqs. 3 and 4 is that the incorporation of cmc can successfully adjust for the effect of solution conditions and surfactant properties, such as salt concentration, solution temperature, hydrocarbon chain length, lateral surfactant interactions, and counterion binding, on surfactant adsorption and thus on corrosion inhibition efficiency.

**MQSAR sub-model.** — It is reported that a nonlinear relationship, QSAR, exists between a series of quantum chemical descriptors, such as HOMO and LUMO energies, and average corrosion inhibition efficiency for a particular surfactant.\(^\text{31-33}\)

\[
\eta(\%) = \frac{(\tilde{A} \cdot \tilde{Q} + \tilde{B} C)}{1 + (\tilde{A} \cdot \tilde{Q} + \tilde{B} C)} \times 100
\]

where \( \tilde{A} \) is a vector of regression coefficients specific to surfactant and solution conditions (such as salt and temperature), \( \tilde{Q} \) is a vector of quantum chemical descriptors for a particular surfactant, and \( \tilde{B} \) is a regression constant. For mixture of homologous surfactants the quantum chemical descriptors are weight-based average values.

Considering that QSAR in Eq. 5 was derived based on LA, it is reasonable that QSAR can also be modified to a general relation to predict \( \eta \) by the incorporation of cmc as presented below:

\[
\eta(\%) = \frac{(\tilde{A}' \cdot \tilde{Q} + \tilde{B}') C}{1 + (\tilde{A}' \cdot \tilde{Q} + \tilde{B}') C} \times 100
\]

where \( \tilde{A}' \) is a modified vector of regression coefficients, and \( \tilde{B}' \) is a modified regression constant. Eq. 6 is termed MQSAR-1, which is similar to MLA in essence and can be adjusted for the effect of solution conditions on corrosion inhibition.

The correlation between salt concentration and cmc of surfactant is well described by the Corrin-Harkins relation as follows:\(^\text{34}\)

\[
\log_{10}(\Gamma) = a' \log_{10}(C_s) + b'
\]

where \( a' \) and \( b' \) are regression constants, and \( C_s \) is salt concentration.

With Corrin-Harkins relation, MQSAR-1 can be further modified to a more general form by eliminated \( \Gamma \) term:

\[
\eta(\%) = \frac{(\tilde{A}' \cdot \tilde{Q} + \tilde{B}') C}{b' C_e^\omega + (\tilde{A}' \cdot \tilde{Q} + \tilde{B}') C} \times 100
\]

where \( \tilde{e} = 10^{b'} \)

Eq. 8 is termed MQSAR-2 and is comparable to MLA and MQSAR-1 with respect to corrosion inhibition efficiency prediction. The advantage of MQSAR-2 is that it does not need the cmc as an input.

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**Table I. Experimental condition for different surfactant testing systems. cmc and sac are estimated values based on experiment.**

| Testing system | Surfactant Mixed ratio | Salt (M) | \( T(\degree C) \) | pH | Electrode | Rotation (RPM) | cmc (\( \mu \text{M} \)) | sac (\( \mu \text{M} \)) | Reference |
|----------------|------------------------|----------|-----------------|----|----------|--------------|-----------------|----------------|-----------|
| I              | C_{14}BzCl/C_{16}BzCl/C_{18}BzCl 0.70/0.25/0.05 | NaCl 0.171 | 40 | 4 | X65 steel | 300 | 140 | 72 | — |
| II             | C_{14}BzCl/C_{16}BzCl/C_{18}BzCl 0.33/0.33/0.33 | NaCl 0.599 | 40 | 5 | X65 steel | 100 | 16.5 | 9 | — |
| III            | AAOA 1                  | NaCl 0.856 | 25 | 6 | 1018 steel | low | 15 | 8.2 | 28, 29 |
| IV             | CPC                     | HC1 1     | 31 | 0 | 1018 steel | 1000 | 1.5 | 1 | 21 |
| V              | C_{16}TAB 1             | Fe(NO_3)_3 0.035 | 32 | — | copper | 1000 | 30 | 22 | 20 |

**Figure 1.** Chemical structure of various surfactant molecules discussed in the present work. \( n \) represents hydrocarbon chain length. AAOA: N-[2-[[2-aminoethyl] amino] ethyl]-9-octadecenamide; C_{14}BzCl: n-benzalkonium chloride; C_{16}E_{20}: polyoxyethylene cetyl ether; CPC: cetylpyridinium chloride; C_{16}TAB: n-alkyl trimethyl ammonium bromide; OG: octylglucoside; SDS: sodium dodecyl sulfate.
**cmc prediction sub-model.**—To use MLA and MQSAR-1 for the prediction of corrosion inhibition efficiency as mentioned above, known value of the cmc for the associated surfactant or mixed surfactants is a prerequisite. A model for the cmc prediction is briefly introduced in this section. More details about model derivation and validation can be found in supplementary information and existing reference.\(^{25}\)

The cmc of surfactant is evaluated using the following equation:

\[
\Gamma = \exp\left(\frac{\Delta \mu_m}{kT}\right)
\]

where \(k\) is Boltzmann constant, \(T\) is temperature, and \(\Delta \mu_m\) is micellization free energy which is estimated from several contributing terms as described below.

\[
\Delta \mu_m = \Delta \mu_h^O + \Delta \mu_{int}^O + \Delta \mu_{pack}^O + \Delta \mu_{at}^O + \Delta \mu_{int}^\Delta + \Delta \mu_{elec}^O + \Delta \mu_{act}^O
\]

where \(\Delta \mu_h^O, \Delta \mu_{int}^O, \Delta \mu_{pack}^O, \Delta \mu_{at}^O, \Delta \mu_{int}^\Delta, \Delta \mu_{elec}^O\), and \(\Delta \mu_{act}^O\) are the free energy contributions from hydrocarbon transfer from water into micelle, formation of micellar core-water interface, hydrocarbon tail packing in the micelle, surfactant headgroup steric interaction, headgroup-counterion mixing, and electrostatic interaction, respectively.\(^{35-36}\) \(\Delta \mu_h^O\) comes from surfactant activity and counterion activity contribution.

Free energy micellization as a function of variables, including on micelle shape, micelle composition, micelle radius, and counterion binding coefficient, at given solution conditions is minimized using home-designed MATLAB code. The minimized micellization free energy is then used for the evaluation of cmc, aggregation number, counterion binding coefficient, and sphere-to-rod transition. Descriptions of model derivation, model parameters including effective area of headgroup or headgroup-ion pair, distance from the surface of the micelle to the center of charged headgroup, Stern layer thickness, as well as related calculations are found in the supplementary information and existing literature.\(^{25,27}\)

With the predicted cmc values of various pure surfactant and mixed surfactants, MLA and MQSAR-1 can be used for the prediction of corrosion inhibition efficiency.

**Experimental**

The homologous cationic benzalkonium chlorides (BAC) surfactants, including benzyl dimethyl dodecyl ammonium chloride (C\(_{12}\)BzCl), benzyl dimethyl tetradecyl ammonium chloride (C\(_{14}\)BzCl), and benzyl dimethyl hexadecyl ammonium chloride (C\(_{16}\)BzCl), were supplied by Sigma-Aldrich Co. LLC with assay values higher than 99%. The molecular structure of the surfactants is optimized and quantum parameters calculated using Gaussian09 simulation package with the method of B3LYP and the basis set of 6-311G(d, p) based on DFT. The test samples for surface tension measurements were prepared by sequential dilution of concentrated aqueous solutions of surfactants using double deionized water, made through a water purification system (Simplicity UV made by EMD Millipore). The stock solution was prepared at a total surfactant concentration of 25 mM for electrochemical measurements using deionized water.

A piece of X65 steel, purchased from Metal Samples, was used as the working electrode in electrochemical measurements with a surface area of 0.196 cm\(^2\). The composition (wt %) is C 0.06%, Mn 1.33%, P 0.007%, S 0.005%, Si 0.30%, Cu 0.30%, Ni 0.10%, V 0.022%, Cr 0.30%, Al 0.019%, Cr 0.05%, Mo 0.03%, Ti 0.017%, Ca 0.0033%, and Fe (balance).

The surface of the X65 electrode was polished using SiC paper in the sequence of 400-600-800-1200 grit and followed by MicroCloth with grit size of ~5 μm supplied by Buchler. A platinum ring electrode and a single junction saturated calomel electrode (SCE) were employed as counter electrode and reference electrode, respectively. Test solutions contained 0.171 or 0.599 M NaCl and were purged with Ar (>99.999%) for 2 hours (hrs) to remove oxygen followed by the purge of CO\(_2\) (>99.999%) for 2 hrs to ensure CO\(_2\) saturation prior to measurements. A flow of CO\(_2\) was maintained during the experiments to keep a positive pressure inside the cell to avoid air ingress. The concentration of dissolved oxygen was monitored before electrochemical measurements using an Oxygen ULR CHEMets Kit and the concentration was measured to be below 20 ppb. The pH was adjusted to 4 - 5 for different mixtures by the injection of 1.0 M NaHCO\(_3\) or diluted HCl into the cell. The surfactants were added at the beginning of each measurement. The test solutions were then kept at open circuit potential (OCP), \(E_{corr}\), for 2 hours for equilibration. Experimental conditions for various testing systems are listed in Table I. For time and experimental resource conservation, only Testing System II is used as an example for the results discussion from electrochemical measurements and for the inhibition efficiency prediction model derivation.

A Gamry reference 600 potentiostat was used for electrochemical measurements. Polarization resistance \(R_p\) was measured using the linear polarization resistance (LPR) method by polarizing the working electrode +/- 0.010 V (SCE) vs. \(E_{corr}\) with a sweep rate of 0.1 mV/s. Potentiodynamic scans were performed with a sweep rate of 1 mV/s from −0.9 V (SCE) to −0.35 V (SCE). Electrochemical impedance spectroscopy (EIS) measurements were made with an applied alternating current (AC) potential of +/-0.010 V rms vs. \(E_{corr}\) in the frequency range of 100,000 - 0.010 Hz. The direct current (DC) potential was set as zero relative to \(E_{corr}\). Each test was repeated at least three times as independent measurements within +/-4% deviation. The collected electrochemical data was analyzed with the Gamry Echem Analyst software package.

The surface tension of test solutions was measured within a precision of 0.1 mN/m by the platinum ring method using a Krüss K10 ST digital tensiometer, equipped with an isothermal vessel holder. All the measurements were performed at a constant temperature of 40°C ± 0.2°C, which has been shown to be higher than the Krafft point of the surfactants and their mixtures in aqueous media containing various concentrations of NaCl. The constant temperature was maintained through a water circulation bath using Polystat temperature controller, purchased from Cole-Parmer. The platinum ring was rinsed with water and heated to an orange color using a Bunsen burner between tests to ensure the complete removal of contaminants. Triplicate measurements were used to confirm reproducibility within +/-2% deviation.

Nova Nano scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) system was used to observe the surface morphology.

**Results and Model Validation**

cmc measurement.—Upon the adsorption of surfactants at the air-water interface, the surface tension is reduced due to the amphiphilic nature of surfactants. Examples of surface tension versus surfactant concentration curves are given in Fig. 2 and the cmc is determined from the interception of the two solid lines in each curve. As can be seen, the surface tension decreases with the increase in surfactant concentration until the surface tension reaches a plateau value, which is a result of surfactant assembled into aggregates, such as micelles, bilayers, or multilayers. Beyond the cmc, additional micelles form but the surface tension remains constant. Fig. 2 also indicates that the cmc of C\(_{12}\)BzCl decreases as the salt concentration increases because more surfactant molecules adsorb on the surface at the higher concentration of salt. The comparison between curves b and c reveals that the ternary mixture of C\(_{12}\)BzCl, C\(_{14}\)BzCl, and C\(_{16}\)BzCl has a lower cmc value because the average hydrocarbon chain length is longer than that of pure C\(_{12}\)BzCl.

Electrochemical measurements.—Considering \(E_{corr}\) stability is important to electrochemical measurements, the X65 steel electrode was immersed in solution and kept at OCP for equilibration before measurement. Examples of the dependence of \(E_{corr}\) of X65 steel electrode on time are given in Fig. 3a. The \(E_{corr}\) stabilized at around
The cmc is around 16.5 after the addition of surfactants at a wide concentration range, which shifts at least one surfactant as anodic or cathodic if the cmc value is indicated by the arrow. The Tafel slopes were estimated from potentiodynamic scan curves. For those curves without anodic Tafel dependence above the cmc, the anodic Tafel slopes were derived from the cathodic branches and cathodic Tafel slopes. The corrosion inhibition efficiency was calculated using Eq. 13 based on the Tafel slope method.

\[ \eta(\%) = 100 \times \frac{i_{\text{corr}} - i_{\text{ocorr}}}{i_{\text{corr}}} \]  

where \( i_{\text{corr}} \) and \( i_{\text{ocorr}} \) are the corrosion current density without and with surfactants in solution respectively.

The calculated Tafel slopes, polarization resistance, corrosion rate, and inhibition efficiency are summarized in Table II for Testing System II. Each electrochemical measurement was repeated at least three times within \( \pm 4\% \) deviation. The corrosion inhibition efficiency results from potentiodynamic scans and LPR match very well. The inhibition efficiency increases rapidly to around 90% with the increase in surfactant concentration from 0 up to 72 \( \mu \text{M} \). Further increase in concentration does not effectively enhance inhibition efficiency even when the concentration is much higher than the cmc. As mentioned previously the concentration of 72 \( \mu \text{M} \) is interpreted as the value of the sac, \( F \), at which a complete monolayer usually forms at the electrode-solution interface, and above which, bilayers or multilayers usually form at the electrode-solution interface. Corrosion inhibition is usually directly related to the electrode surface coverage. Therefore, the monolayer is effective with respect to corrosion protection and the formation of bilayers and multilayers do not contribute much to additional corrosion inhibition beyond the protection provided by monolayer coverage.

The topography of a corroded X65 steel electrode surface was examined using SEM as shown in Fig. 4. The electrode surface was strongly damaged in the absence of surfactants in corrosive solution, as shown in Fig. 4a. In contrast, there was much less damage on the...
Table II. Results obtained from polarization resistance measurements and potentiodynamic scans for X65 in absence and presence of various total concentrations of surfactants in Testing System II.

| C (µM) | βa (mV dec⁻¹) | βc (mV dec⁻¹) | icorr (µA cm⁻²) | η (%)⁴⁺ | Rp (ohm cm⁻²) | η (%)⁵⁺ |
|--------|----------------|----------------|-----------------|---------|--------------|---------|
| 0      | 55.2 ± 2       | 202 ± 6        | 182 ± 7         | 0       | 101 ± 4      | 0       |
| 1.5    | 51.7 ± 2       | 212 ± 7        | 90 ± 3          | 51 ± 2  | 197 ± 7      | 49 ± 2  |
| 3      | 57.3 ± 3       | 221 ± 7        | 47 ± 2          | 74 ± 3  | 408 ± 10     | 75 ± 3  |
| 4.5    | 56.5 ± 2       | 205 ± 5        | 39 ± 2          | 79 ± 3  | 483 ± 10     | 79 ± 3  |
| 6      | 49.7 ± 1       | 212 ± 4        | 27 ± 2          | 85 ± 2  | 636 ± 12     | 84 ± 3  |
| 9      | 49.2 ± 2       | 210 ± 2        | 20 ± 1          | 89 ± 2  | 850 ± 15     | 88 ± 2  |

⁴⁺η (%) calculated from potentiodynamic scans using Tafel slopes; ⁵⁺η (%) calculated from LPR.

electrode surface with surfactant addition. Moreover, the electrode was better protected with higher concentration of surfactants.

**Determination of parameter K’ in MLA sub-model.** The corrosion current density as a function of (C/Γ) for various testing systems is presented in Fig. 5a. As can be seen the current density decreases rapidly with the increase in surfactant concentration in the range between 0 and the sac for each of the testing systems. Above the sac, the current density reaches a plateau value. Fig. 5a also indicates that the surfactants in Testing Systems IV and V are not as effective in corrosion inhibition as those surfactants in Testing Systems II and III due to relatively higher plateau values of current density in the concentration range studied.

Fig. 5b presents the plots of 1/θ versus 1/C based on the regular LA in the concentration range between 0 and the cmc for various testing systems. The calculated adsorption free energies based on Eqs. 1 and 2 are −45.6 kJ/mol for Testing System II, −43.4 kJ mol⁻¹ for Testing System III, −44.1 kJ mol⁻¹ for Testing System IV, and −37.9 kJ mol⁻¹ for Testing System V. If adsorption free energy is more positive than −20 kJ mol⁻¹, the interaction between surfactant and metal is usually dominated by physisorption. If adsorption free energy is more negative than −40 kJ mol⁻¹, the interaction is usually dominated by chemisorption in which the adsorption involves charge sharing or transfer between surfactant molecules and metal surface to form coordination bonds.⁴³⁻⁴⁴ Based on the calculated adsorption free energy, it is inferred that the surfactant adsorption in Testing Systems II, III, and IV is dominated by chemisorption; the surfactant...
adsorption in Testing Systems V is dominated by both physiosorption and chemisorption. However, physiosorption can sometimes be energetically favorable and significant whereas chemisorption may sometimes have relatively weak binding energy due to various factors that influence adsorption.45,46

Over the entire range of surfactant concentration, the linear fitting is excellent based on the regular LA model for each investigated system in Fig. 5b. In contrast, the MLA model features a sharp transition around the sac as shown in Fig. 5c. Below the sac, there is a plateau as the concentration increases. The transitions indicate that below the sac the inhibition efficiency increases rapidly with the increase in surfactant concentration and that further increase in concentration above the sac does not effectively enhance inhibition efficiency even when the concentration is much higher than the cmc. These results are in accordance with electrochemical measurements. For each testing system, the linear part (\(C < \text{sac}\)) of the plot in Fig. 5c is presented in Fig. 5d, in which the value of the modified adsorption constant \(K^*\) is given by the slope of the linear fitting equation. The \(K^*\) values are 13.97, 15.73, 0.96, and 4.84 for Testing System II, III, IV, and V, respectively. The fitted \(K^*\) value will be used for the corrosion inhibition prediction model discussed in this paper. Note that homologous surfactants tend to achieve similar levels of surface coverage at similar ratios of surfactant concentration to surfactant cmc, so the value of \(K^*\) does not vary much for homologous surfactants.48 Considering the surfactant used in Testing Systems I and II are homologous, \(K^* = 13.97\) can be directly used in Testing System I.

**Determination of parameters \(\hat{A}'\) and \(\hat{B}'\) in MQSAR sub-model.**—For better illustration of adsorption of BAC surfactants on steel surface, regular quantum chemical descriptors,19,20,31-34 including the energies of molecular frontier orbitals \(E_{\text{HOMO}}\) and \(E_{\text{LUMO}}\), energy difference between HOMO and LUMO \((\Delta E)\), Mulliken charge distribution on the backbone atoms, dipole moment of the surfactant molecule \(\mu\), surface electrostatic potential based on electron density of the molecule, and the fraction of electrons transferred from the surfactant to the steel surface \(\Delta N\) were determined based on DFT using Gaussian09. HOMO tends to donate electrons to suitable acceptor substances on the steel surface while LUMO tends to accept electrons from the steel surface and lower LUMO energy usually indicates stronger electron accommodation.19,20,47 The energy gap \(\Delta E\) usually characterizes the stability of the complex of surfactant and metal surface.31,48,49 The value of \(\Delta N\) describes the inhibition achieved from electron donation.31,49 The Mulliken charges and surface electrostatic potential usually shed light on the electron distribution in surfactant molecules and electrostatic interaction between surfactant and iron or steel.30-31 The molar volume of surfactant molecule, \(V_{\text{sm}}\), is also needed to be considered due to its potential effect on surfactant packing/aggregation efficiency and steric interactions. However, the relationship between dipole moment and corrosion inhibition is still a controversial issue.31,45

Many existing literature articles illustrate in detail how to calculate the fraction of electrons transferred from inhibitor to the metal surface, \(\Delta N\).31,49 The calculation process is briefly described below. The ionization potential \(E_{\text{ip}}\) and the electron affinity \(A_{\text{e}}\) are approximately \(-E_{\text{HOMO}}\) and \(-E_{\text{LUMO}}\), respectively. The absolute electronegativity \(\chi\) and the global hardness \(\Upsilon\) are defined as

\[
\chi = \left( E_{\text{ip}} + A_{\text{e}} \right) / 2
\]

\[
\Upsilon = \left( E_{\text{ip}} - A_{\text{e}} \right) / 2
\]

\(\Delta N\) is given by

\[
\Delta N = \frac{\chi_{\text{met}} - \chi_{\text{inh}}}{2 (\Upsilon_{\text{met}} - \Upsilon_{\text{inh}})}
\]

where \(\chi_{\text{met}}\) and \(\Upsilon_{\text{met}}\) are electronegativity and global hardness of metals (electrodes), respectively, \(\chi_{\text{inh}}\) and \(\Upsilon_{\text{inh}}\) are electronegativity and global hardness of surfactant molecule, respectively. The reported electronegativity and global hardness of iron (4.06 eV/mole and 3.81 eV/mole)\,49,50 are used. For Testing System V, the electronegativity and global hardness of copper are 5.59 eV/mole and 0.15 eV/mole, which were calculated using Gaussian09 considering the same procedures for surfactants.

The values of quantum descriptors of homologous BAC surfactants as well as surfactants in other testing systems are summarized in Table III. For qualitative illustration of homologous BAC surfactants, the calculated results of C12BzCl are presented in Fig. 6 considering that the electronic properties of homologous series should be similar. Application of Eqs. 5, 6, and 8 based on electrochemical data of Testing System II in Table II and calculated quantum descriptors in Table III yields the following semi-empirical equations of QSAR, MQSAR-1, and MQSAR-2, respectively:

\[
\eta (\%) = \left( \frac{3.97 E_{\text{HOMO}} + 5.05 E_{\text{LUMO}} - 10.12 \Delta E + 51.71 \Delta N + 18200 \mu + 0.417 V_{\text{sm}} + 574693}{1 + (3.97 E_{\text{HOMO}} + 5.05 E_{\text{LUMO}} - 10.12 \Delta E + 51.71 \Delta N + 18200 \mu + 0.417 V_{\text{sm}} + 574693)} \right) \times 100
\]

\[
\eta (\%) = \left( \frac{-4.80 E_{\text{HOMO}} - 0.656 E_{\text{LUMO}} - 2.41 \Delta E + 1.15 \Delta N - 0.052 \mu - 0.071 V_{\text{sm}} + 2.01}{1 + (-4.80 E_{\text{HOMO}} - 0.656 E_{\text{LUMO}} - 2.41 \Delta E + 1.15 \Delta N - 0.052 \mu - 0.071 V_{\text{sm}} + 2.01)} \right) \times 100
\]

\[
\eta (\%) = \left( \frac{-30.3 E_{\text{HOMO}} - 2.06 E_{\text{LUMO}} + 10.1 \Delta E - 2.50 \Delta N - 0.213 \mu - 0.004 V_{\text{sm}} + 2.22}{1 + (-30.3 E_{\text{HOMO}} - 2.06 E_{\text{LUMO}} + 10.1 \Delta E - 2.50 \Delta N - 0.213 \mu - 0.004 V_{\text{sm}} + 2.22)} \right) \times 100
\]

Note that Eq. 18 and Eq. 19 are comparable with respect to corrosion inhibition efficiency prediction. Similar to the above mentioned MLA sub-model, the regression parameters of \(\hat{A}' = (-4.80, -0.656, -2.41, 1.15, -0.052, -0.071)\) and \(\hat{B}' = 2.01\) in Eq. 18, which are the values from one fitting operation using the experimental data of Testing System II, can be directly used in other testing systems with homologous surfactants or similar surfactants for corrosion inhibition evaluation. Without using the cmc in QSAR, the transfer of the regression parameters \(\hat{A} = (3.97, 5.05, -10.12, 51.71, 18200, 0.417)\) and \(\hat{B} = 574693\) in Eq. 17 to other testing systems is expected to fail in the evaluation of corrosion inhibition because the surfactant interaction effect is not taken into account.

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**Table III. Quantum chemical descriptors of various surfactants in the solvent of pure water.**

| BAC   | \(E_{\text{HOMO}}\) (eV) | \(E_{\text{LUMO}}\) (eV) | \(\Delta E\) (eV) | \(\mu\) (debye) | \(\Delta N\) | \(V_{\text{sm}}\) (cm\(^2\)/mol) |
|-------|-----------------|-----------------|--------------|-------------|---------|-----------------|
| C12BzCl | -5.186          | -5.141          | 0.045        | 0.057       | 343.9   | 150             |
| C14BzCl | -5.174          | -5.050          | 0.124        | 0.057       | 265.8   | 100             |
| AAOA   | -5.314          | -6.189          | 0.875        | 0.133       | 352.3   | 100             |
| CPC    | -5.994          | -3.609          | 2.384        | -0.012      | 253.9   | 100             |
| C16TAB | -7.178          | -7.122          | -0.056       | 6.953       | -4.399  | 335.2           |
MLA sub-model and MQSAR sub-model validation.— To validate the MLA sub-model and the MQSAR sub-model, and to illustrate the advantage of MLA relative to LA, and of MQSAR relative to QSAR, examples of the applications of Eqs. 1 and 4, and Eqs. 17 and 18 to Testing System I are presented in Fig. 7. Note that the values of thermodynamic parameter $K_{ad}$ in Eq. 1, and fitting parameters $K'$ in Eq. 4, $\bar{A}$ and $B$ in Eq. 5, and $\bar{A}'$ and $B'$ in Eq. 6 are calculated based on experimental data of Testing System II. The calculated value of $K_{ad}$ is $7.28 \times 10^5$ M$^{-1}$. The values of other parameters are as mentioned in previous sections. The predicted cmc value $\Gamma$ of mixed surfactants in Testing System I is $1.44 \times 10^{-4}$ M which is used in the validation of MLA sub-model.

Note that the average chain length, salt concentration, and testing conditions (such as pH) are different for Testing System I and Testing System II. As can be seen from Fig. 7, the predicted corrosion inhibition efficiency using both MLA sub-model and MQSAR-1 sub-model agree well with experimental results due to the adjustment of solution environment, surfactant interactions, and surfactant chain length etc. through cmc. The prediction using LA and QSAR, however, deviates significantly from experimental data. Note that MQSAR-2 is similar to MQSAR-1 in essence and thus is not shown in the comparison in Fig. 7.

As discussed above, both MLA and MQSAR need the cmc value of surfactant or surfactant mixture of discussed as an input. The validation of the well-developed cmc prediction model is exemplified in Fig. 8. The predicted cmc for pure, binary- and ternary-mixed BAC surfactants in the solution containing various NaCl concentrations agree well with experimental results as shown in Figs. 8a–8c. For all of the discussed testing systems listed in Table I, there is excellent agreement in the value of cmc between prediction and experiment (Fig. 8d). The application of the cmc prediction model to the binary mixture of anionic and nonionic surfactants (Fig. 8e) and to the ternary mixture of cationic, cationic, and nonionic surfactants (Fig. 8f) is also successful, even though the agreement between the prediction and the experiment is not as excellent as that shown in Figs. 8a–8d. Note that the experimental data of Testing Systems III, IV and V is cited from references 21,52–56.

It is expected that the integrated model based on the MLA sub-model and the cmc sub-model or the integrated model based on the MQSAR sub-model and the cmc sub-model should be successful in the prediction of corrosion inhibition efficiency of the discussed surfactant systems. The prediction of the predicted results from the integrated model and from the experimental measurements is shown in Fig. 9, based on the data of corrosion inhibition from all the five testing systems as summarized in Table IV. The prediction agrees very well with experiment for Testing Systems I, II, III, and IV. The deviation for Testing System V is slightly higher but still falls within a reasonable range. This may be due to less effective monolayer coverage of C$_{16}$TAB on copper surface in presence of slightly complicated salt Fe(NO$_3$)$_3$ in Testing System V. Note that the MQSAR predicted corrosion inhibition of all the five testing systems are based on Eqs. 18 and 19 with unified fitting parameters, which indicates the vastly improved applicability and robustness of developed MQSAR over regular QSAR.

Discussion

It can be seen in Table III that all the three surfactants display slight differences in quantum descriptors. In the context of simple corrosion inhibition it is believed that alkyl chains are chemically unreactive...
substituents and that the homologous surfactants which vary only in alkyl chain length have very similar quantum descriptors. In other words, these quantum descriptors, calculated based on frontier orbital theory with a very strong fundamental basis, describe the characteristics of the head groups and reflect the associated adsorption properties. It is feasible to get quantum descriptors from only one type of surfactant and then apply these parameters to a series of homologous surfactants or surfactants with similar headgroups. In addition, the quantum descriptors of mixtures regardless of surfactant classes.

Figure 8. (a) cmc of pure cationic BAC surfactants (C\(_n\)BzCl) as a function of NaCl concentration in solution at \(T = 40^\circ C\); (b) cmc of ternary mixed BAC surfactants (C\(_{12}\)BzCl/C\(_{14}\)BzCl/C\(_{16}\)BzCl = 0.7/0.25/0.05) as a function of NaCl concentration in solution at \(T = 40^\circ C\); (c) cmc of ternary mixed BAC surfactants as a function of bulk mixed molar fraction of C\(_{14}\)BzCl at NaCl concentrations of 0.0342 M, 0.171 M, or 0.856 M at \(T = 40^\circ C\); C\(_{12}\)BzCl & C\(_{16}\)BzCl are equal-molar mixed; (d) comparison of predicted (Pre.) and experimental (Exp.) cmc of discussed surfactants in various testing systems in Table I; (e) cmc of binary mixed anionic and nonionic surfactants (SDS and OG) as a function of mixed bulk solution composition of OG with 20 mM NaCl at \(T = 25^\circ C\); (f) cmc of ternary mixed cationic, cationic, and nonionic surfactants (C\(_{16}\)BzCl, C\(_{16}\)TAB, and C\(_{16}\)E20) at various mixed molar ratios with 30 mM NaCl in solution at \(T = 25^\circ C\). For Figs. 8(a, b, c, and e) symbols represent experimental data; lines represent model predicted data. Experimental data of testing systems III, IV, and V is cited from references. 21,52–56

Figure 9. Comparison (90 data points in total) of model predicted inhibition efficiency and experimental inhibition efficiency of pure surfactant and mixed surfactants in various testing systems listed in Table I. The associated corrosion inhibition efficiency is summarized in Table IV. Experimental data of Testing systems III, IV, and V is cited from references. 21,22,28,29

In this study, the molar-based average was used to calculate the quantum descriptors of mixtures regardless of surfactant classes.

The cmc model takes into account the ion/salt effect on aggregation/adsorption, the effect of chain length of surfactant, van der Waals interactions between surfactant molecules, steric interactions between head groups, electrostatic interactions at interfacial region of micelles, and the interactions between solvent and surfactant. 21,22,25,27,35,57 Therefore, the insertion of cmc into QSAR or LA can accurately describe the adsorption phenomena of surfactants on substrate (metal electrode) and associated effects of physical and chemical properties of surfactants and solvent environment. Mixtures of surfactants, which involve surfactant of the same or different classes, have been widely used in practical applications because of their superior physicochemical properties, capabilities, and/or economic viability. 15,16 Beyond the applicability of our model for pure surfactant and mixed homologous surfactants, the more valuable part lies in its potential to evaluate the corrosion inhibition of various surfactant mixtures of different classes at various solution conditions using only one set of experimental data.

The fitting of MQSAR only requires one set of experimental data just as MLA does. The only difference is that the fitting of MQSAR yields a set of regression parameters simultaneously but MLA only has one parameter. In terms of the number of regression parameters, the use of MLA is simpler. In other words, the MQSAR is an alternative to the MLA for corrosion inhibition modeling.

It is interesting to note that the regression parameters in QSAR/MQSAR for one class of surfactants may be transferred to other surfactants with similar head groups or similar quantum descriptors. Similarly, the MLA parameter (\(K^*\)) for one surfactant can be used for other surfactants with similar head groups. In addition, the parameters of one surfactant mixture can be used for the mixtures of similar surfactants. The initial evaluation of transferability of regression parameters was performed by applying Eqs. 18 and 19 to the five testing systems discussed and the results in Fig. 9 indicates...
1. Monolayer coverage of pure surfactant or mixed surfactants in resources. The University of Utah is acknowledged for providing computational

5. The developed corrosion inhibition prediction models provide a good agreement between experimental data and various model predictions. Other cases of parameter transfer between different classes of surfactants can be found elsewhere.58

4. The incorporation of the cmc into MLA, MQSAR-1, and MQSAR is provided as an alternative to the MLA for the predic-

tions. Other cases of parameter transfer between different classes

3. MQSAR-1 successfully accounts for the effect of solution en-

vironment, such as salt concentration and surfactant interactions, and the effect of surfactant properties on surfactant adsorption and thus on corrosion inhibition efficiency. The integrated prediction model is efficient in predicting corrosion inhibition of surfactants in various discussed testing systems.

5. The developed corrosion inhibition prediction models provide potential methods to evaluate the effectiveness of various surfactant or surfactant mixtures in corrosion inhibition under various testing conditions.

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References

1. M. Finiglar and J. Jackson, Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: A review. Corrosion Sci., 86, 17 (2014).

2. A. Popova, M. Christov, and A. Vasilev, Mono- and dicaticonic benzothiazolic quater

nary ammonium bromides as mild steel corrosion inhibitors. Part III: Influence of the temperature on the inhibition process. Corrosion Sci., 94, 70 (2015).

3. K. S. George and S. Nešić, Investigation of carbon dioxide corrosion of mild steel in the presence of acetic acid—part 1: basic mechanisms. Corrosion, 63(2), 178 (2007).

4. Y. Zhou and Y. Zuo, The intergranular corrosion of mild steel in CO\textsubscript{2}+NaNO\textsubscript{2} solution. Electrochim. Acta, 154, 157 (2015).

5. G. A. Zhang and Y. F. Cheng, On the fundamentals of electrochemical corrosion of X65 steel in CO\textsubscript{2} containing formation water in the presence of acetic acid in petroleum production. Corrosion Sci., 51, 87 (2009).

6. B. R. Linter and G. T. Burstein, Reactions of pipeline steels in carbon dioxide solution. Corrosion Sci., 44(1), 117 (1999).

7. N. G. Thompson, Y. Mark, and D. Daniel, Cost of corrosion and corrosion mainte-
nance strategies, Corrosion Rev., 25, 247 (2007).

8. Z. Xia, K. C. Chou, and Z. S. Smialowska, Pitting corrosion of carbon steel in CO\textsubscript{2}-containing NaCl brine. Corrosion, 45(8), 636 (1989).

9. M. B. Kermanni and A. Morshed, Carbon dioxide corrosion in oil and gas production—a compendium. Corrosion, 59(8), 659 (2003).

10. P. Bai, H. Zhao, S. Zheng, and C. Chen, Initiation and development stages of steel corrosion in wet H\textsubscript{2}S environments. Corrosion Sci., 93, 109 (2015).

11. M. Z. A. Rafiquee, S. Khan, N. Saxena, and M. A. Qurashi, Investigation of some oleochemicals as green inhibitors on mild steel corrosion in sulfuric acid. J. Appl. Electrochem., 39(8), 1409 (2009).

12. M. A. Qurashi, A. Singh, V. K. Singh, D. K. Yadav, and A. K. Singh, Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of Murraya koenigii leaves. Mater. Chem. Phys., 122(1), 114 (2010).

13. J. O. Bockris and A. K. N. Reddy, Modern Electrochemistry, 2nd ed., Kluwer Aca-
demic/Plenum Publishers, New York (2000).

14. A. Kokalj, S. Peljhan, M. Finsgar, and I. Milosev, What determines the inhibition effectiveness of ATA, BTAH, and BTAOH corrosion inhibitors on Copper? J. Am. Chem. Soc., 132(46), 16657 (2010).

15. R. M. Hill, Mixed Surfactant systems, Marcel Dekker, New York (1993).

16. M. J. Rosen, Surfactants and Interfacial Phenomena, 3rd ed., John Wiley, New York (2004).
17. S. K. Sonu, A. K. Tiwari, and S. K. Saha, Study on mixed micelles of cationic gemini surfactants having hydroxyl groups in the spacers with conventional cationic surfactants: effects of spacer group and hydrocarbon tail length. *Ind. Eng. Chem.* 30(2), 123 (2022).

18. S. Nelić, Key issues related to modelling of internal corrosion of oil and gas pipelines – A review. *Corrosion Sci.*, 49(12), 4308 (2007).

19. I. B. Obot, D. D. Macdonald, and Z. M. Gasem, Density functional theory (DFT) as a powerful tool for designing new organic corrosion inhibitors. Part 1: An overview. *Corrosion Sci.*, in press.

20. G. Gece, The use of quantum chemical methods in corrosion inhibitor studies. *Corrosion Sci.*, 50(11), 2981 (2008).

21. M. L. Free, W. Wang, and D. Y. Ryu, Prediction of corrosion inhibition using surfactants. *Corrosion*, 60(9), 837 (2004).

22. W. Wang and M. L. Free, Prediction and measurement of corrosion inhibition of mild steel using nonionic surfactants in chloride media. *Corrosion*, 46(10), 2601 (2004).

23. M. L. Free, A new corrosion inhibition model for surfactants that more closely accounts for actual adsorption than traditional models that assume physical coverage is proportional to inhibition. *Corrosion Sci.*, 46(12), 3101 (2004).

24. M. L. Free, Understanding the effect of surfactant aggregation on corrosion inhibition of mild steel in acidic medium. *Corrosion Sci.*, 44(12), 2865 (2002).

25. Y. Zhu, M. L. Free, and G. Yi, Electrochemical measurement, modeling, and prediction of corrosion inhibition efficiency of ternary mixtures of homologous surfactants in electrolyte solution. *Corrosion Sci.*, 98, 417 (2015).

26. M. A. Migahed, M. A. Hegazy, and A. M. Al-Sabagh, Synergic inhibition effect between Cu2+ and cationic gemini surfactant on the corrosion of downhole tubing steel during secondary oil recovery of old wells. *Corrosion Sci.*, 61, 10 (2012).

27. Y. Zhu and M. L. Free, Electrochemical Measurement and Modeling of Corrosion Inhibition Efficiency of Surfactants in Salt Solutions. *ECS Transactions*, (2015).

28. M. P. Desimone, G. Gordillo, and S. N. Simson, The effect of temperature and concentration on the corrosion inhibition mechanism of an amphiphilic amido-amino in CO2 saturated solution. *Corrosion Sci.*, 53, 4033 (2011).

29. M. P. Desimone, G. Gudmeier, G. Gordillo, and S. N. Simson, Amphiphilic amido-amino as an effective corrosion inhibitor for mild steel exposed to CO2 saturated solution: polarization, EIS, and PM-IRRAS studies. *Electrochim. Acta.*, 56, 2990 (2011).

30. W. Durnic, R. De Marco, A. Jefferson, and B. Kinsella, Development of a structure-activity relationship for oil field corrosion inhibitors. *J. Electrochem. Soc.*, 146(5), 1751 (1999).

31. M. Ghoshali, I. Dunase, M. H. Maddahy, and M. RashvandAvei, Correlated ab initio and electroanalytical study on inhibition behavior of Z-Mercaptobenzothiazole and its thio-thiole thia-tautomerism effect for the corrosion of steel (API SL XS2) in sulphuric acid solution. *Ind. Eng. Chem.*, 52(2), 14875 (2013).

32. L. Lukovits, E. Kalman, and F. Zacchi, Corrosion inhibitors correlation between electronic structure and efficiency. *Corrosion*, 57(1), 3 (2001).

33. K. F. Khaleed, Experimental and theoretical study for corrosion inhibition of mild steel in hydrochloric acid solution by some new hydrazine carbodithioic acid derivatives. *Appl. Surf. Sci.*, 252(12), 4120 (2006).

34. M. L. Corrin and W. D. Harkins, The effect of salts on the critical concentration for the formation of micelles in colloidal electrolytes. *J. Am. Chem. Soc.*, 69(3), 683 (1947).

35. L. Moreira and A. Firoozabadi, Molecular thermodynamic modeling of specific ion effects on micellization of ionic surfactants. *Langmuir*, 21(12), 9850 (2005).

36. A. Goldsipe and D. Blankschtein, Modeling counterion binding in ionic-nonionic and ionic-zwitterionic binary surfactant mixtures. *Langmuir*, 21(22), 9850 (2005).

37. M. Knag, K. Bilkova, E. Gulbrandsen, P. Carlsen, and J. Sjöblom, Langmuir-Blodgett films of docosylthiobetaineammonium bromide and octadecanol on iron. Deposition and corrosion inhibitor performance in CO2 containing brine. *Corrosion Sci.*, 48, 2592 (2006).

38. O. L. Riggs, *Corrosion Inhibitors*, 2nd ed., C. C. Nathan, Editor, Houston, TX (1973).

39. D. A. Jones, *Principles, Prevention of Corrosion*, Macmillan Publishing Company (1991).

40. V. Ivancicovic, S. Ramachandran, and P. Prince, Inhibition of carbon dioxide corrosion of mild steel by imidazole and their precursors. *Corrosion*, 55(5), 309 (1999).

41. Y. R. Dong and M. L. Free, The importance of temperature and viscosity effects for surfactant adsorption measurements made using the electrochemical quartz crystal microbalance. *J. Coll. Int. Sci.*, 264(2), 402 (2003).

42. Y. R. Dong and M. L. Free, The use of electrochemical quartz crystal microbialance and surface tension measurements for the determination of octylamine and cetylpyridinium chloride adsorption in sodium chloride solutions. *Colloids Surf. A: Physicochem. Eng. Asp.*, 226(1-3), 17 (2003).

43. M. Christov and A. Popova, Adsorption characteristics of corrosion inhibitors from corrosion rate measurements. *Corrosion Sci.*, 46(7), 1613 (2004).

44. P. O. Ofatok and Y. Zheng, Synergic inhibition behaviour of methylbenzyl quaternary imidazole derivative and iodide ions on mild steel in H2SO4 solutions. *Corrosion Sci.*, 51(4), 850 (2009).

45. X. Shi, R. Zhang, C. Minot, K. Hermann, M. A. Van Hove, W. Wang, and N. Lin, Complex molecules on a flat metal surface: large distortions induced by chemisorption can make physiosorption energetically more favorable. *J. Phys. Chem. Lett.*, 1 (19), 2974 (2010).

46. J. N. Israelachvili, *Intermolecular and Surface Forces*, 3rd ed., Academic Press, San Diego, 2011.

47. D. A. Winkler, M. Breedon, A. E. Hughes, F. R. Burden, A. S. Barnard, T. G. Harvey, and I. Cole, Towards chromate-free corrosion inhibitors: structure–property models for organic alternatives, *Green Chem.*, 16, 3349 (2014).

48. M. L. Free, W. Wang, and P. Prince, Inhibition of carbon dioxide corrosion in sulphuric acid solution by ketoconazole: Experimental and theoretical investigation, *Corrosion Sci.*, 52(1), 198 (2010).

49. R. Yildiz, An electrochemical and theoretical evaluation of 4,6-diamino-2-pyrimidinethiol as a corrosion inhibitor for mild steel in HCl solutions, *Corrosion Sci.*, 90, 544 (2015).

50. L. Li, X. Zhang, S. Gong, H. Zhao, B. Qi, L. Li, and L. Ji, The discussion of the descriptors for the Qsar model and molecular dynamics simulation of benzimidazole derivatives as corrosion inhibitors. *Corrosion Sci.*, (2015).

51. M. Sabir, G. Gee, F. Karci, and S. Bilge, Experimental and theoretical study of the effect of some heterocyclic compounds on the corrosion of low carbon steel in 3.5% NaCl medium. *J. Appl. Electrochem.*, 38(6), 809 (2008).

52. K. Shinoda, *The critical micelle concentration of soap mixtures (two component mixture). J. Phys. Chem.*, 58(7), 541 (1954).

53. K. Shinoda and T. Nakagawa, *Colloidal Surfactants*, Academic Press, New York (1963).

54. K. Kanemaya, A. Muroya, and T. Takagi, Properties of a mixed micellar system of sodium dodecyl sulfate and octylglycocide. *J. Colloid Interface Sci.*, 196(1), 48 (1997).

55. H. P. Moises de Oliveira and M. H. Gehlen, Characterization of mixed micelles of sodium dodecyl sulfate and tetraoctylthylene dodecyl ether in aqueous solution. *Langmuir*, 18(10), 3792 (2002).

56. A. A. Dar, G. M. Rather, S. Ghosh, and A. R. Das, Micellation and interfacial behavior of binary and ternary mixtures of model cationic and nonionic surfactants in aqueous NaCl medium. *J. Colloid Interface Sci.*, 322(2), 572 (2008).

57. S. Ramachandran, B. Tsai, M. Blanco, H. Chen, Y. Tang, and W. A. Goddard, Self-assembled monolayer mechanism for corrosion inhibition of iron by imidazolines, *Langmuir*, 12(26), 6419 (1996).

58. H. Zhao, X. Zhang, L. J. H. Hu, and Q. Li, Quantitative structure–activity relationship model for amino acids as corrosion inhibitors based on the support vector machine and molecular design. *Corrosion Sci.*, 83, 261 (2014).

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