Experimental Investigation and Modeling of the Performance of Pure and Mixed Surfactant Inhibitors: Partitioning and Distribution in Water-Oil Environments

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A critical model of water-oil surfactant distribution has been developed and validated for the evaluation of mixed surfactant partitioning and distribution in water-oil environments. The surfactant distribution model, which is a combination of surfactant partitioning sub-model, partitioning coefficient calculation method, and a developed critical micelle concentration (cmc) prediction sub-model based on previous work, provides a very powerful tool to evaluate the partitioning of mixed surfactants in water-oil environments. Different methods to calculate partitioning coefficients are introduced, which includes transfer free energy method and group contribution method. The partitioning data from model prediction and from experiment agree very well. The mixed micelles start to form in water-oil environments only after the apparent cmc is reached during partitioning. The selective partitioning of one particular surfactant in mixed surfactants can be explained by its apparent cmc which is interpreted as one characteristic of the hydrophobicity/hydrophilicity of that surfactant in water-oil environments. It is believed that the partitioning and distribution of non-homologous mixed surfactants in oil-water environments are evaluated theoretically and experimentally for the first time. The effect of partitioning on corrosion inhibition of mixed surfactants was initially evaluated by modified Langmuir adsorption and by electrochemical measurements. The corrosion inhibition efficiency from model prediction and from experimental measurements is comparable.

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Manuscript submitted August 13, 2015; revised manuscript received September 23, 2015. Published September 26, 2015.

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 prevent corrosive media penetration and attack.1–4 Compared to the production and use of pure surfactants, surfactant mixtures are well known due to the superior physicochemical properties and capabilities in efficient solubilization, adsorption, suspension, and transportation.5–8 The solutions of surfactant mixtures can often be conveniently tuned to achieve desired properties by adjusting the mixed surfactant types and molar ratios. More surface-active and expensive surfactants are often mixed with less surface-active and cheaper surfactants to reduce cost.9,10 Natural mixtures of surfactants are sometimes used to avoid the investment in separation processes. However, further studies are required in order to optimize inhibition efficiency of surfactant mixtures and minimize environmental impact.

Surfactant molecules have hydrophilic and hydrophobic sections,7,11,12 which are critical to the adsorption on metal surface and associated corrosion inhibition.9–12 The hydrophilic functional group of surfactant molecules strongly prefers interaction with polar entities such as metals, which is helpful in corrosion inhibition. The hydrophobic portion, which is non-polar, strongly prefers interaction with hydrophobic entities such as hydrocarbon phase. Because of this, surfactant molecules tend to escape from polar environments, such as the water, by associating and aggregating hydrocarbon chains together, which compromises the surfactant adsorption on metal surface and corrosion inhibition efficiency.

When an aqueous surfactant solution comes into contact with an immiscible organic liquid in one environment, such as water-oil-metal pipe environments, surfactant monomers may prefer partitioning into the organic liquid until equilibrium is reached.13–15 which usually depletes the surfactants available in the aqueous phase for adsorption on the metal surface and for corrosion inhibition.4 Considering the behavior of surfactant partitioning in oil-water environments and associated interfacial phenomena, the determination of surfactant partitioning between water and oil usually serves as the basis of the hydrophobic-hydrophilic balance13,14,16,17 and is critical for the evaluation of corrosion inhibition efficiency of surfactants.3

For pure surfactant, the partitioning is usually characterized by the partitioning coefficient, which is defined as the ratio of monomeric surfactant concentration in oil to that in aqueous phase.14,16,18,19 Extensive research has been performed on low concentration (typically lower than aqueous critical micelle concentration (cmc)) partitioning of nonionic surfactants,14,16,17,20–27 The partitioning research on higher surfactant concentration solutions, however, has been rarely reported and is limited.19,28–30 Relevant reports on the partitioning of ionic surfactant at high concentration level are even less.31 The investigation of partitioning above the aqueous cmc (meaning no oil phase) and apparent cmc is important (the apparent cmc is the average concentration in water-oil environments of pure or mixed surfactants at which micelles start to form): the partitioning is a monomer process, and the partitioning coefficient is determined by monomer concentrations in two phases, which are limited by micelle formation.

For mixed surfactants, the phenomenon becomes more complicated. The effect of individual mixed species on the partitioning, and the adsorption of each surfactant at the oil/water interface involves many factors. It has been shown that for most pure surfactants, a plateau concentration of monomer is reached either in the oil phase or in the aqueous phase with increasing total surfactant concentration beyond the aqueous cmc.9,12,15 However, it is also reported that for mixed surfactants the amount of surfactants partitioned into the oil phase continues to increase beyond the aqueous cmc.19,30,32 The different partitioning behavior of mixed surfactants above the aqueous cmc is reported to arise from the selective partitioning of more hydrophobic components into the oil phase, which makes the experimental investigation and quantitative modeling work more challenging.19,29,32

In the present research, a water-oil surfactant distribution model is proposed to evaluate the associated water-oil partitioning phenomena of mixed surfactants. This model is applicable over a wide total surfactant concentration range, including the aqueous cmc, oil cmc, and apparent cmc. The model inputs are the aqueous cmc of pure surfactant, total surfactant concentration, water and oil volume ratio, and mixed molar ratio in bulk solution, the last three of which are known partitioning conditions. The partitioning coefficient can either be directly measured from experiment or calculated from different methods that are introduced below. The aqueous cmc can also be measured from experiment. However, it usually can be calculated from well-developed prediction models that have been introduced

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Water-Oil Surfactant Distribution Model

Surfactant partitioning sub-model derivation.— A mass balance of total mixed surfactants in the water-oil environment is (see List of Symbols for symbol definition)

\[ C_{\text{tot}}V_w = \bar{C} (V_w + V_o) \]  

[1]

When \( \bar{C} < \Gamma_{\text{app}} \), mass balance of each mixed surfactant \( i' \) at partitioning equilibrium is given by

\[ x_iC_{\text{tot}}V_w = C_{\text{mi}}V_w + C_oV_o \]

[2]

where \( \bar{C} \) is the overall concentration of mixed surfactants in water-oil environment and \( \Gamma_{\text{app}} \) is the apparent cmc of the surfactant mixture in water-oil environment.

Alternatively,

\[ x_i = \frac{C_{\text{mi}}V_w + C_oV_o}{C_{\text{tot}}V_w} \]

[3]

The partitioning coefficient of pure surfactant \( i' \) is defined as

\[ K_i = \frac{C_{\text{mi}}}{C_w} \]

[4]

Partitioning coefficient of surfactant mixture is termed apparent partitioning coefficient and is given by

\[ K_{\text{mix}} = \frac{C_o}{C_m} = \sum \frac{C_{\text{mi}}}{C_m} \]

[5]

Substitution of Eqs. 3 and 4 into Eq. 5 leads to

\[ K_{\text{mix}} = \frac{\sum x_i/(V_w + V_o K_i)}{\sum x_i/(V_w + V_o K_i)} \]

[6]

Eqs. 2–3 and 5–6 are only applicable to the condition of \( \bar{C} < \Gamma_{\text{app}} \), whereas, Eq. 4 applies to all values of \( \bar{C} \).

When \( \bar{C} > \Gamma_{\text{app}} \), it is assumed that partitioning process between water and oil only involves monomers. For ionic surfactant, the partitioning involves the surfactant molecule and the associated counterion. On the other hand, there is no dissociation in the process of partitioning.

The chemical potential of monomeric surfactant \( i' \) in water and oil phase, and the chemical potential of counterion \( j' \) in water can be written, respectively, as

\[ \mu_i^w = \mu_i^{w_0} + RT \ln \left( \frac{\gamma_m^{w_0}}{\gamma_m^{w_0 c_m}} \right) \approx \mu_i^{w_0} + RT \ln \left( \frac{C_{\text{mi}}}{C_{\text{mw}}} \right) \]

[7]

\[ \mu_i^o = \mu_i^{o_0} + RT \ln \left( \frac{\gamma_m^{o_0}}{\gamma_m^{o_0 c_m}} \right) \approx \mu_i^{o_0} + RT \ln \left( \frac{C_{\text{mi}}}{C_{\text{mo}}} \right) \]

[8]

\[ \mu_j^w = \mu_j^{w_0} + RT \ln \left( \frac{\gamma_m^{w_0}}{\gamma_m^{w_0 c_m}} \right) \approx \mu_j^{w_0} + RT \ln \left( \frac{C_{\text{mio}}}{C_{\text{mw}}} \right) \]

[9]

The chemical potential of surfactant \( i \) in mixed micelles is given by

\[ \mu_i^m = \mu_i^{m_0} + RT \ln (f_i a_i) \]

[10]

When micelles form, a saturation concentration for monomer is reached both in the water and oil phases. Therefore, when partitioning equilibrium between micelle and water is reached for surfactant \( i' \), the chemical potential of surfactant \( i' \) in mixed micelles are equal to the sum of the chemical potential of surfactant \( i' \) and the chemical potential of associated counterion \( j' \) in water

\[ \mu_i^m = \mu_i^{w_0} + RT \ln \left( \frac{C_{\text{mi}}}{C_{\text{mw}}} \right) + \delta_i \mu_j^w \]

[11]

where \( \delta_i \) represents binding coefficient of counterion \( j' \) to micelles. Note that ionic surfactant is assumed to be completely dissociated when dissolved in aqueous phase as a monomer but in the micelles form the surfactant is associated to some extent with a counterion. Therefore, \( \delta_i = 0 \) for micelles of nonionic surfactant and \( 0 < \delta_i < 1 \) for micelles of ionic surfactant.

The cmc is interpreted as the monomer concentration at saturation for surfactant \( i' \). Considering the equilibrium condition among pure micelles, water, and oil phases for surfactant \( i' \), we have

\[ \mu_i^{m_0} = \mu_i^{w_0} + RT \ln \left( \frac{\gamma_m^{w_0}}{\gamma_m^{w_0 c_m}} \right) + \delta_i \mu_j^w \]

[12]

With Eqs. 7, 8, and 10–12, it is obtained

\[ C_{\text{mi}} = f_i a_i \Gamma_i^w \]

[13]

\[ C_m = f_i a_i \Gamma_i^o \]

[14]

Molar fraction of surfactant \( i' \) in mixed micelles is written as

\[ \alpha_i = \frac{x_iC_{\text{mi}}V_w}{C_{\text{mi}} - C_mV_w + C_mV_o} \]

[15]

Substitution of Eqs. 13 and 14 into Eq. 15 and arrangement leads to

\[ \alpha_i = \frac{x_iC_{\text{mi}}V_w}{C_{\text{mi}} - C_m(1 + V_o/V_w) + f_i \Gamma_i^w + f_i \Gamma_i^w V_w/V_w} \]

[16]

Summation of the molar fraction of surfactant \( i' \) in the mixed micelle should be unity

\[ \sum \alpha_i = 1 \]

[17]

and thus

\[ \sum \frac{x_iC_{\text{mi}}V_w}{C_{\text{mi}} - C_m(1 + V_o/V_w) + f_i \Gamma_i^w + f_i \Gamma_i^w V_w/V_w} = 1 \]

[18]

For fixed values of other parameters, Eq. 18 is a polynomial function of \( C_m \). For surfactant mixtures with multiple components, \( C_m \) has multiple corresponding mathematical values. However, in reality \( C_m \) should only have one value and should be confined in the range of

\[ \Gamma_{\text{app}} < C_m < \bar{C} \]

[19]

Eqs. 18 and 19 are solved simultaneously with respect to \( C_m \) using designed MATLAB code. The value of \( \Gamma_{\text{app}} \) can be calculated using the method described below.

At the mixed cmc the following equations apply

\[ x_i \Gamma_{\text{app}} (V_w + V_o) = C_{\text{mi}}V_w + C_mV_o \]

[20]

\[ \frac{x_i \Gamma_{\text{app}} (V_w + V_o)}{f_i \Gamma_i^w V_w + f_i \Gamma_i^w V_w} = \frac{C_{\text{mi}}V_w + C_mV_o}{f_i \Gamma_i^w V_w + f_i \Gamma_i^w V_w} \]

[21]

The sum of Eqs. 13 and 14 leads to

\[ C_{\text{mi}}V_w + C_mV_o = \alpha_i \left( f_i \Gamma_i^w V_w + f_i \Gamma_i^w V_w \right) \]

[22]

Replacement of mole fraction of surfactant \( i' \) in micelles using Eq. 17 and rearrangement yield

\[ \sum C_{\text{mi}}V_w + C_mV_o = \alpha_i \left( f_i \Gamma_i^w V_w + f_i \Gamma_i^w V_w \right) = 1 \]

[23]
Combination of Eqs. 21 and 23 and rearrangement leads to
\[
\sum x_i \Gamma_{\text{app}}(V_w + V_o) f_i \Gamma_i V_w + f_i \Gamma_i V_o = 1
\]  
[24]
Rearrangement leads to
\[
\Gamma_{\text{app}} = \frac{1}{\sum f_i \Gamma_i V_w/(x_i V_w + V_o) + f_i \Gamma_i V_o/(x_i V_w + V_o)}
\]  
[25]

The above derivation is a general form of the partitioning sub-model. However, some surfactants may not form micelles in both aqueous phase and in oil phase when \( C > \Gamma_{\text{app}} \). If there is no micelle formation in the aqueous phase, \( \Gamma_i^w \) should be replaced by \( \Gamma_i^w / K_i \); if there is no micelle formation in the oil phase, \( \Gamma_i^o \) should be replaced by \( \Gamma_i^o K_i \). It is also important to be aware that \( \Gamma_i^w \) can still be replaced using \( \Gamma_i^w K_i \) even if micelles form in the oil phase provided that \( \Gamma_i^o \) is in isolated aqueous phase that can be measured from experiment or predicted from existing models. Here the isolated aqueous phase means the aqueous phase is not in contact with the oil phase and there is no partitioning process. The activity coefficient, \( f_i \), of surfactant \( 'i' \), arises from the interaction between surfactant molecules, which is considered by the cmc prediction sub-model (see following sections).35,38 and therefore it is assumed be unity in the present research without any compromise of the overall model performance.

**Partitioning coefficient determination method.**— The partitioning sub-model requires the input of the partitioning coefficient of surfactant \( 'i' \), which can be determined from experimental measurement (see Eq. 4) or from model estimation. Here, one model is briefly introduced for the estimation of partitioning coefficient.

As previously mentioned, the chemical potential of surfactant \( 'i' \) in water and in oil should be equal at partitioning equilibrium:
\[
\mu_i^w = \mu_i^o
\]  
[26]
Substitution of Eqs. 7 and 8 leads to
\[
\mu_i^{w,o} + RT \ln \left( \frac{\gamma_i^{w,o} C_i^{w,o}}{\gamma_i^{w,o} C_i^{w,o}} \right) = \mu_i^{w,o} + RT \ln \left( \frac{\gamma_i^{w,o} C_i^{w,o}}{\gamma_i^{w,o} C_i^{w,o}} \right)
\]  
[27]
Standard free energy change of transfer of surfactant \( 'i' \) from aqueous phase to oil phase is given by
\[
\Delta \mu_i^{w,o} = \mu_i^{w,o} - \mu_i^{w,o}
\]  
[28]
Combination of Eqs. 4, 27, and 28 leads to
\[
\Delta \mu_i^{w,o} = RT \ln \left( \frac{\gamma_i^{w,o} C_i^{w,o}}{\gamma_i^{w,o} C_i^{w,o}} \right)
\]  
[29]
Further rearrangement leads to
\[
\frac{K_i}{\gamma_i^{w,o} C_i^{w,o}} = \exp \left( \frac{-\Delta \mu_i^{w,o}}{RT} \right)
\]  
[30]
where \( \gamma_i^{w,o} \) is assumed to be unity, and \( C_i^{w,o} \) and \( C_i^{w,o} \) are molar concentration of oil and water, respectively. The essence of \( \gamma_i^{w,o} \) is to take into account the effect of dissolved salt in water on water-oil partitioning of surfactants.

For ionic surfactant,
\[
\gamma_i^{w} = \sqrt{\gamma_i^{w,o} \gamma_i^{w,o}}
\]  
[31]

For nonionic surfactant,
\[
\gamma_i^{w} = \gamma_i^{w,o}
\]  
[32]
Where \( \gamma_i^{w,o} \) is the functional headgroup activity coefficient and \( \gamma_i^{w,o} \) is the hydrocarbon chain tail activity coefficient. \( \gamma_i^{w,o} \) can be calculated from Pitzer’s method36,37 or the Davies equation.36 \( \gamma_i^{w,o} \) is estimated from the Setchenov equation shown as below.
\[
\gamma_i^{w,o} = 10^{h_i L_i}
\]  
[33]
Where \( I \) is ionic strength of solution. \( k_i \) is the Setchenov coefficient specific to added salt in water.39,40

The standard transfer free energy \( \Delta \mu_i^{w,o} \) can be determined by different methods. Two methods are briefly described below.

**Method I**: free energy transfer method. \( \Delta \mu_i^{w,o} \) is the sum of two contributing parts: head group part \( \Delta \mu_{\text{h,head}} \) and hydrocarbon tail part \( \Delta \mu_{\text{h,tail}} \). The first part is the transfer free energy of hydrocarbon tail from salt water to organic phase, which is calculated in two steps using the reported methodology for alkanes.35,40

Step one is the transfer of hydrocarbon chain from salt water to pure water:
\[
\frac{\Delta \mu_{\text{h,tail}}^{w,o}}{RT} = -k_i L_i C_i
\]  
[34]
Step two is the transfer of hydrocarbon chain from pure water to oil/organic phase:
\[
\frac{\Delta \mu_{\text{h,tail}}^{w,o}}{RT} = \frac{\Delta \mu_{\text{h,head}}^{w,o}}{RT} + (L_i - 1) \frac{\Delta \mu_{\text{h,head}}^{w,o}}{RT}
\]  
[35]
\[
\frac{\Delta \mu_{\text{h,head}}^{w,o}}{RT} = 3.38 \ln T + \frac{4064}{T} - 44.13 + 0.025957 T
\]  
[36]
\[
\frac{\Delta \mu_{\text{h,head}}^{w,o}}{RT} = 5.85 \ln T + \frac{896}{T} - 36.15 - 0.0056 T
\]  
[37]

The second part is the transfer free energy of the headgroup, which is estimated either from reported experimental data24,25,41-44 or from quantum calculation as summarized in Table I. The quantum calculation of transfer free energy of headgroups followed the reported procedure,4 in which the transfer free energy \( \Delta \mu_{\text{h,head}}^{w,o} \) is interpreted as the difference in solvation energy of surfactant ‘i’ in oil and in water based on the quantum chemical calculations using Gasussian99.

**Method II**: group contribution method, in which the aqueous solubility of a molecule is empirically related to structural descriptors.45 The transfer free energy contribution of each group in a molecule to its solubility is calculated. The sum of free energy contribution of all groups is considered as the free energy of transfer.45,46

Once the standard transfer free energy of surfactant ‘i’ from aqueous phase to oil phase is calculated based on the methods described above, the partitioning coefficient can be determined using Eq. 30 at given conditions of water-oil environment.

**cmc prediction sub-model.**— The aqueous cmc of pure surfactant or mixed surfactants in the absence of oil phase is usually very close to the aqueous cmc in the presence of non-polar oil phase, which is confirmed for the discussed surfactants in the present work by experiment. On the other hand, the non-polar oil phase does not contribute to the micelle formation in the aqueous phase. It is actually reported that for nonionic surfactants with non-polar organic as oil phase, such as heptane and toluene, the aqueous cmc has been observed to be very similar to the corresponding cmc without oil phase47 and that for certain anionic surfactants with nonpolar organic (such as heptane) as the oil phase, the aqueous cmc has also been found to be very close to the cmc measured in water in the absence of oil.48 For certain cationic surfactants with polar oil phase (dichloromethane), however, the aqueous cmc is significantly different from the corresponding cmc with oil phase.49

As previously discussed, the cmc of each mixed surfactant component in aqueous phase is required as an input. The required cmc values can either be measured using traditional methods, such as surface tension measurement and conductivity measurement, or be predicted using a simplified molecular thermodynamic model44 or a more advanced molecular thermodynamic model.35 The advanced cmc sub-model is briefly described below.

The aqueous cmc of mixed surfactants (taken as one example) is evaluated using the following equation:
\[
\Gamma = (C_{iin} + C_{iext}) \exp \left( \frac{\Delta \mu_{\text{h,head}}^{w,o}}{RT} \right)
\]  
[38]
where \( k \) is Boltzmann constant, \( T \) is temperature, and \( \Delta \mu_{\text{h,head}}^{w,o} \) is micellization free energy, which is estimated from several contributing
Table I. Standard transfer free energy of functional groups from aqueous phase to organic phase.

| surfactant | structure | functional group | organic phase | T, °C | Energy, kJ/mol | Reference |
|------------|-----------|------------------|---------------|-------|----------------|-----------|
| BAC        | ![BAC structure](image) | ![Functional group](image) | Toluene       | 40    | 55.7           | Present work |
|            |           |                  |               | 50    | 54.3           |           |
|            |           |                  |               | 60    | 52.7           |           |
| Polyoxethylene glycol n-dodecyl ether (C12En) | ![Polyoxethylene glycol structure](image) | ![Functional group](image) | isooctane | 25   | 2.61           | 24         |
| Primary alcohol ethoxylate (C12OEn) | ![Primary alcohol structure](image) | ![Functional group](image) | heptane | 20   | 2.68           | 29,41,43   |
|            |           |                  |               |       |                |           |
| N-based alkyl amines and derivatives* | ![N-based alkyl amine structure](image) | ![Functional group](image) | Heptane | 20   | 6.04           | Present work, 42-44 |
|            |           |                  |               |       |                |           |
| Alkyl ether isosorbide (CnIsoendo/exo) | ![Alkyl ether isosorbide structure](image) | ![Functional group](image) | cyclohexane | 25   | 27.1           | 25         |
|            |           |                  |               |       |                |           |

* Simplified chemical formula is used in Fig. 4c. For example, CnNH2 represents CnH(2n+1)NH2.
terms as described below.

$$\Delta \mu^i_{\text{act}} = \Delta \mu^i_{\text{elec}} + \Delta \mu^i_{\text{int}} + \Delta \mu^i_{\text{pack}} + \Delta \mu^i_{\text{st}} + \Delta \mu^i_{\text{act}}$$

where $\Delta \mu^i_{\text{elec}}$, $\Delta \mu^i_{\text{int}}$, $\Delta \mu^i_{\text{pack}}$, $\Delta \mu^i_{\text{st}}$, and $\Delta \mu^i_{\text{act}}$ 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, electrostatic interaction, and surfactant activity and counterion activity contribution, respectively. \(^{[39]}\) Details of the cmc prediction sub-model can be found elsewhere. \(^{[35]}\)

The developed cmc prediction sub-model takes into account hydrocarbon chain length, head group steric interactions, van der Waals force between surfactant molecules, electrostatic force between micelles and monomeric surfactant, and entropy of mixing. The cmc sub-model takes into account the ion/salt effect on surfactant aggregation, the effect of chain length, van der Waals interactions between surfactant molecules, steric interactions between head groups, electrostatic interactions at the interfacial region of micelles, and the interactions between solvent and surfactant.

By the integration of partitioning sub-model, partitioning coefficient calculation method, and the cmc prediction sub-model, the water-oil surfactant distribution model is developed. With this developed model, partitioning coefficient $K_{i}$ of surfactant 'i', the aqueous cmc of surfactant 'i', the apparent cmc of mixed surfactants in water-oil environment, $\Gamma_{\text{ppp}}$, monomer concentration of surfactant 'i' in water and in oil phase, $C_{\text{mm}}$ and $C_{\text{oo}}$, and molar fraction of surfactant 'i' in the mixed micelles, $\alpha_i$, can be predicted at given inputs, which include total surfactant concentration $C_i$ and mixed molar ratio $\chi$, in bulk solution. If no experimental data is available, the methods introduced above can be used to predict the aqueous cmc and partitioning coefficient values and the values can be substituted into the surfactant distribution model.

**Experimental**

All the chemicals were used as received. The homologous cationic benzalkonium chlorides (BAC) surfactants, including benzyl dimethyl dodecyl ammonium chloride (C12 or C12), benzyl dimethyl tetradecyl ammonium chloride (C14 or C14), and benzyl dimethyl hexadecyl ammonium chloride (C16 or C16), and polyoxyethylene n-ethyl ether (CnEOn) were supplied by Sigma-Aldrich Co. LLC with assay values higher than 99%. Primary alcohol ethoxylate (C12EO6) was provided by Witco Corporation. Benzyl dimethyl tetradecyl ammonium d7 chloride (C14−) was provided by Santa Cruz Biotechnology with compound purity higher than 98% and isotopic purity higher than 99%.

For the partitioning tests, equal volumes (5 ml) of aqueous phase and oil phase (toluene or hexane) were separately added to a partitioning cell. The cell is a glass cylinder, one inch in diameter, which has two ports (top and bottom) for the sampling of oil and aqueous phase separately without contamination from each other. The cell was kept in a water bath at the desired temperatures (25, 40, 50, and 60° C) for at least 12 hours. Gentle stirring (25–30 rpm) using a magnetic stirrer was applied for to accelerate partitioning equilibration but prevent emulsification. In this study it was confirmed that the partitioning equilibrium is reached within 12 hours. The constant temperature was maintained through a water circulation bath using a Polylab temperature controller, purchased from Cole-Parmer. The initial concentration of pure surfactant or mixed surfactants in aqueous phase is known. No surfactant was initially added to the oil phase. The aqueous phase contains different concentrations of NaCl (0, 0.03, 0.032, 0.17, 0.599, 0.804, and 0.856 M). The sampled aqueous and oil phases were centrifuged following partitioning equilibration and were then injected into a liquid chromatography instrument for analysis.

The sample analysis was conducted using an Ultra Performance Liquid Chromatography (Waters ACQUITY) coupled with a UV detector and a triple quadruple mass spectrometer (Waters TQD). The separation was performed with a 100 × 2.1 mm i.d. (1.7 um) Acquity UPLC BEH C18 column purchased from Waters. The flow rate was controlled at 0.6 ml/min and the target column temperature was maintained at 40 °C. The mobile phase consisted of water and acetonitrile with 0.1% formic acid. Ionization was performed with an electrospray source in positive mode and acquisition was achieved in multiple reactions monitoring (MRM).

The data analysis was performed using MassLynx 4.1 Software. The internal calibration method was adopted for quantification. The C14− was used as internal references at constant concentration of 5 × 10−7 M in all tested samples (added after partitioning and before liquid chromatography and mass spectrometry analysis) and standard samples. The concentration of standard solution for tested surfactants ranged between 2.5 × 10−4 M and 2.5 × 10−5 M. All the tested aqueous samples were diluted to this calibration range for partitioning equilibrium quantification. Surfactant concentration at equilibrium in oil phase is calculated based on a mass balance. Note that surfactant concentration of certain oil samples was also determined experimentally for verification. Triplicate measurements were conducted for each sample and at least three samples were tested for each surfactant concentration level.

A dynamic light scattering instrument “Wyatt DynoBro NanoStar” was used for the detection of surfactant aggregation in the oil phase. Triplicate measurements were performed for each sample and at least two samples were tested for each surfactant concentration level to assure the reproducibility. The detection temperature was controlled at the same temperature as partitioning tests.

The experimental cmc was obtained from surface tension measurements. 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. 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). All measurements were performed at desired constant temperatures, which have been confirmed to be higher than the Krafft point of the surfactants and their mixtures in aqueous media. 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 organic contaminants. Triplicate measurements were conducted to confirm reproducibility for each sample.

In the electrochemical measurements, 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 cm². 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 0.046%, 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 abraded using SiC paper in 500-600 grit and was polished using MicroCloth with a particle size of ~5 μm supplied by Buehler. A platinum ring electrode and a single junction saturated calomel electrode (SCE) were employed as counter and reference electrodes, respectively.

The glass cell of 150 mL volume for electrochemical measurements is designed with a water jacket for isothermal testing. Aqueous solutions in the cell for tests contained 0–1 M NaCl and were purged with Ar (>99.999%) for 2 h to remove oxygen followed by a purge of CO2 (>99.999%) for 2 h to ensure CO2 saturation prior to measurements. The concentration of dissolved oxygen was monitored before electrochemical measurements using an Oxygen ULR CHEMets Kit, and the concentration was measured and found to be below 20 ppb. The pH was adjusted to 4–5 for different mixtures by the addition of 1.0 M NaHCO3 or diluted HCl. The three electrodes and pH meter were in direct contact with the aqueous phase in the glass cell during equilibration and measurements. The surfactants were added to the aqueous phase at the beginning of each measurement. The effect of partitioning and aggregation on steel corrosion rate and on corrosion inhibition efficiency of inhibitors was evaluated by the addition
of desired volume of toluene into the cell following the addition of surfactants. Care was taken to ensure that the added toluene did not contact the electrodes. The working electrode was rotated at very low speed (25–30 rpm) considering the rotation can facilitate partitioning process but the speed was not high enough to cause microemulsions. For the electrochemical tests without toluene, the step for the addition of toluene was skipped.

A Gamry reference 600 potentiostat was then used for electrochemical measurements. Polarization resistance $R_p$ was measured every 20 minutes in 15 hours 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 for the evaluation of corrosion rate as a function of time. At the end of the 15-hour measurement, potentiodynamic scans (PDS) were performed with a sweep rate of 1mV/s from $−0.9$ V (SCE) to $−0.35$ V (SCE). Electrochemical impedance spectroscopy (EIS) measurements were then 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. Each test was repeated at least three times as an independent measurement. The collected electrochemical data were analyzed using software package Gamry Echem Analyst. Corrosion current density and charge transfer resistance was calculated from each measured potentiodynamic scan curve and Nyquist plot, respectively. The average current density and resistance was calculated from each measured potentiodynamic scan and Nyquist plot, respectively. The average current density and the average corrosion inhibition were calculated for each surfactant concentration level.

Results and Discussion

Surfactant distribution model validation.—Fig. 1 shows the calibration curves based on internal reference $C_{14}$ for the three homologous BAC surfactants between the concentrations of $2.5 \times 10^{-8}$ M and $2.5 \times 10^{-5}$ M. As can be seen, the linearity of the calibration curves over three orders of magnitude is excellent for all three surfactants. Based on the experimental data, the concentration of all tested samples was higher than $2.5 \times 10^{-4}$ M. For samples with concentrations higher than $2.5 \times 10^{-5}$ M, dilution was applied, which assured the accuracy of quantitative determination of surfactant concentration in the aqueous phase at equilibrium. Surfactant concentration at equilibrium in the oil phase was calculated based on mass balance within the error of 5% as mentioned previously.

The partitioning results of pure BAC surfactants, C12, C14, and C16, in water-oil partitioning are shown in Fig. 2a. The experimental partitioning coefficients at 40°C are 0.041 for C12, 0.598 for C14, and 8.802 for C16, respectively. The equilibrium concentration of pure surfactant in aqueous phase increases linearly with the initial concentration up to around the aqueous cmc, which is consistent with previous reports.20,32,33 Above the aqueous cmc, extra C12 and C14 accumulated in aqueous phase, as indicated by the arrow for C14, for example. Extra C16 partitioned into the oil phase probably because of stronger hydrophobicity. It is inferred that C12 and C14 form micelles in the aqueous phase but not in the oil phase, whereas C16 mainly forms inverse micelles in the oil phase and the cmc of C16 in the oil phase is estimated at $1.08 \times 10^{-4}$ M, which is calculated using the value of $1.2 \times 10^{-4}$ M minus $1.2 \times 10^{-5}$ M. Note that $1.2 \times 10^{-4}$ M is the highest value of C16 and that $1.2 \times 10^{-5}$ is the saturation value of concentration of C16 in aqueous phase before micellization of C16 in water-oil partitioning process at 40°C, as indicated by the arrows in Fig. 2a.

The temperature effect on the water-oil partitioning of C16 was also investigated. As can be seen in Fig. 2a, the equilibrium concentration in aqueous phase decreases with increasing temperature, which means K16 increases with increasing temperature.

The thermodynamic relation between entropy, enthalpy, and free energy of transfer is given by:

$$\Delta v_{mi}^p = \Delta H_{mi}^p - T \Delta S_{mi}^p$$

Combination of Eqs. 29 and 40 leads to

$$\ln K_1 = \frac{\Delta H_{mi}^o}{RT} + \frac{\Delta S_{mi}^o}{R} + \ln \left( \frac{\gamma_{mi}^o C_{mi}}{\gamma_{mi}^o C_{mi}} \right)$$

Figure 2. (a) Equilibrium concentration $C_{14}^w$ vs. initial concentration $C_{10b}$ of pure BAC surfactants in 0.171 NaCl aqueous phase at equilibrated water-oil partitioning at different temperatures. Solid lines are the linear fittings before micellization for the determination of partitioning coefficient. Arrow in (a) indicates the linear-to-nonlinear transition for C14. (b) Partitioning coefficient of C16 versus 1/T. Solid line is the linear fitting.
It is assumed that the values of $\Delta H^\circ_{tr}$ and $\Delta S^\circ_{tr}$ do not vary much within the temperature range of discussed. The plot of $\ln K_1$ vs. $1/T$ is a straight line, which yields a slope for the calculation of $\Delta H^\circ_{tr}$ and an intercept for the calculation of $\Delta S^\circ_{tr}$, as shown in Fig. 2b. The calculated entropy and enthalpy of C16 partitioning are 0.203 kJ/(mol·K) and 53.9 kJ/mol. The calculated free energy of transfer is $-9.64, -11.67, \text{ and } -13.69$ kJ/mol at 40, 50, and 60°C, respectively. It is thus concluded that at the temperature range of interest the partitioning of C16 is in favor of the oil phase and the partitioning coefficient increases with increasing temperature. In combination with Eqs. 34–37 as introduced in the Method I, the transfer free energy of the C16 functional head group $\Delta \mu^\circ_{C16}$ can be calculated and summarized as presented in Table I. The values of $\Delta \mu^\circ_{C16}$ are used for the following calculation of partitioning coefficients of BAC surfactants under various partitioning conditions.

The aggregation properties of BAC surfactants in toluene were examined using dynamic light scattering (DLS). Fig. 3 presents the DLS testing results, including aggregate radius and intensity of collected light signal, of C12, C14, and C16 in toluene, which was sampled from the oil phase at the water-oil partitioning equilibrium of pure BAC surfactants. As can be seen, both the particle radius and signal intensity of C12 and C14 barely changed in the concentration range evaluated, which indicates C12 and C14 in toluene do not form micelles. For C16, however, micelles started to form at the added initial concentration of around $1.20 \times 10^{-4}$ M, as indicated both by the aggregate radius and by the intensity. These results support the findings in Fig. 2 that C12 and C14 form micelles in aqueous phase while C16 mainly forms inverse micelles in oil phase. According to Fig. 3a, the diameter of micelles of C16 (assumed as spherical micelles) is estimated to be 0.45 nm, which is close to twice the extended length of the hydrocarbon tail of C16 (2.17 nm). The extended length of the hydrocarbon tail is calculated using a group contribution of 0.1265 nm for methylene and 0.2765 nm for the methyl group.

The comparison of predicted partitioning coefficient and experimental partitioning coefficient of pure BAC surfactants (C12, C14, and C16) in water (salt containing) – oil environment is shown in Fig. 4a. The predicted partitioning coefficients at various conditions based on the transfer free energy calculated using the two aforementioned methods match the experimental data reasonably well. Note that the transfer free energy of the polar functional group of BAC surfactants is 55.3 kJ/mol at 40°C, which is based on the partitioning coefficients of C16 as shown in Fig. 2 and the associated calculations. This value is much lower than the reported value of the polar functional group ($>\text{N(CH}_3\text{)}_2^+$) transferring from 0.1 M aqueous sodium hydroxide to heptane. This is probably because the functional group in BAC surfactants has one extra benzene group and one extra methylene group, which prefer the non-polar organic phase and thus decrease the free energy of transfer. The affinity of the functional group to different organic phases also contributes to the energy difference.
In Method II, the transfer free energy of a surfactant molecule is estimated from the solubility, which is calculated from a few contributing groups, including -CH< and >C< in a ring, -CH2- and CH3- in linear alkane, and -N-. The predicted partitioning coefficients from Method I will be used in the overall partitioning model because it deviates less from experimental results.

The method to determine the transfer free energy for the partitioning coefficient was also tested on other surfactants. Fig. 4b presents the predicted and experimental partitioning coefficients of homologous polyoxyethylene glycol n-dodecyl ether C12H25(OCH2CH2)nOH (or C12E<) surfactants in pure water and isooctane environments; Fig. 4c presents the predicted and experimental partitioning coefficients of N-based alkyl amines and derivatives in 0.1 M NaOH water and heptane environments. As can be seen, there is an excellent agreement between predicted and experimental partitioning coefficients.

The partitioning model requires the aqueous cmc of pure surfactant as input as discussed previously. The aqueous cmc in isolated aqueous phase can either be determined from experimental measurement or predicted from the existing model.34,35 In experimental measurement, the aqueous cmc in isolated aqueous phase is calculated from the interception of the two solid lines in the curve of surface tension versus surfactant concentration as shown in Fig. 5a. As can be seen, the surface tension decreases with the increase in surfactant concentration until the surface tension reaches a plateau value, which is the result of surfactant assembled into aggregates, such as micelles, bilayers, or multilayers. Alternatively, the aqueous cmc can be predicted from the well-developed model based on our previous work.34,35 The comparison of the measured cmc and the predicted cmc of pure BAC surfactants as a function of NaCl concentration in aqueous phase is shown in Fig. 5b. The predicted cmc values will be used in the partitioning model. Note that the predicted cmc of C16 in 0.171 M NaCl aqueous phase is 1.20 × 10−5 M, which is very close to the oil cmc of C16 divided by partitioning coefficient, 1.08 × 10−4 M/8.802 = 1.22 × 10−5 M. It is confirmed by experiment that the aqueous cmc of surfactants in isolated aqueous phase can be used in the partitioning model and that the oil cmc can be calculated using the aqueous cmc and partitioning coefficient, rather than using direct measurement from experiment.

As previously discussed, the use of the surfactant distribution model in water and oil phases requires the inputs of the aqueous cmc of surfactant “i”, volume ratio, total surfactant concentration, and mixed molar ratio in bulk solution. With all required inputs provided, the model application to the water-oil partitioning of equal-molar ternary mixtures of BAC surfactants is shown in Fig. 6. Figs. 6a and 6b present equilibrium concentrations of monomeric surfactants in water and in oil versus total initial concentration of mixed surfactants added to the aqueous phase. The intersection of the vertical dashed line and horizontal axis identifies the aqueous cmc of surfactant mixture, which is Γ<sup>W</sup> = 3.40 × 10−5 M. As can be seen, the partitioning of each mixed component as well as the overall partitioning continues without any change when C<sub>tot</sub> reaches Γ<sup>W</sup>. This is consistent with the reported view of surfactant mixture in aqueous phase: 2Γ<sup>W</sup>.
that the amount of surfactants partitioned into the oil phase continues to increase beyond the aqueous cmc of that mixture.\textsuperscript{19,29,32} It is easy to understand that the partitioning of surfactants into the oil phase depletes the surfactants in the aqueous phase to an extent that causes micelles to fail to form in the aqueous phase at \( C_{\text{tol}} < 2\Gamma_{\text{app}} \). 2\( \Gamma_{\text{app}} \) is used as the upper limit rather than \( \Gamma_{\text{app}} \) considering that water and oil are equal-volume mixed and that the horizontal axis represents the total initial concentration of surfactants, \( C_{\text{tol}} \), added to the aqueous phase.

Above \( 2\Gamma_{\text{app}} \), which is suggested by the dotted line, the partitioning behavior of each mixed surfactant component starts to change as indicated by the transition point in Figs. 6a–6c. The mixed surfactants form micelles in aqueous phase as indicated by Fig. 6c. It is also interesting to observe that above the transition point, monomeric concentrations of \( C_{14} \) and \( C_{16} \) in both phases decrease while the concentrations of more hydrophilic \( C_{12} \) in both phases continue to increase to some extent, and that the total monomeric concentration in aqueous phase (\( C_{\text{w}}^n \)) increases and the counterpart in oil (\( C_{\text{tol}}^n \)) phase decreases slightly before reaching a plateau. This phenomenon can be explained by the fact that surfactant molecules in micellar form are generally more thermodynamically stable than existing in monomeric form with respect to relatively hydrophobic species and that \( C_{16} \) and \( C_{14} \) prefer to exist in micellar form, which leads to the leveling off of monomeric surfactant concentration in water and oil phases. The preference of micellar form of \( C_{16} \) and \( C_{14} \) is reflected by the much higher molar fraction in micelles at the beginning of micelle formation as shown in Fig. 6d, indicating the formation of more hydrophobic micelles at the beginning. As the total surfactant concentration increases, the micelles become less hydrophobic.

The molar fraction change of \( C_{12} \), \( C_{14} \), and \( C_{16} \) in mixed micelles seems to be contrary to the report that more hydrophilic micelles form at first and then become more hydrophobic as the total initial concentration \( C_{\text{tol}} \) increases for mixed surfactants in a water-oil system.\textsuperscript{29,51} However, the relative hydrophobicity/hydrophilicity in one-phase system, such as in water phase, may or may not be the same as that in a two-phase system, such as in the water-oil phases for one particular surfactant relative the other. The hydrophobicity/hydrophilicity of surfactant can usually be reflected by the value of the cmc in the environment discussed. To clarify this statement, the apparent cmc of pure surfactant ‘\( i \)’ in water-oil environment is defined as

\[
\Gamma_{\text{app},i} = \frac{\Gamma_{\text{w},i} V_w + \Gamma_{\text{tol},i} V_{\text{tol}}}{\alpha_i (V_w + V_{\text{tol}})} \quad \text{[42]}
\]

If \( \Gamma_{\text{w},i} \) is not available, \( \Gamma_{\text{w},i} \) is replaced with \( \Gamma_{\text{w},i} K_i \); if \( \Gamma_{\text{tol},i} \) is not available, \( \Gamma_{\text{tol},i} \) is replaced with \( \Gamma_{\text{tol},i} / K_i \) as stated previously. This defined apparent cmc of one pure surfactant in water-oil environment can reflect the relative hydrophobicity/hydrophilicity of that surfactant. The higher the apparent cmc of one pure surfactant, the lower the hydrophobicity of that surfactant in water-oil environments. The reverse is also true.

For mixed BAC surfactants in water-oil environments, the apparent cmc of each mixed component is calculated based on aqueous cmc and partitioning coefficient, and the relative values are shown below.

\[
\Gamma_{\text{app}, C_{12}} > \Gamma_{\text{app}, C_{14}} > \Gamma_{\text{app}, C_{16}} \quad \text{[43]}
\]

Therefore, \( C_{16} \) is still the most hydrophobic surfactant among the three in water-oil environments, as well as in water only. It is thus easy to understand that \( C_{16} \) has the highest mixed molar fraction at the beginning of micelle formation in water-oil environments, followed by the mixed molar fractions of \( C_{14} \) and \( C_{12} \). As \( C_{14} \) increases, the molar fraction \( \alpha_i \) in mixed micelles of each mixed component approaches the initial mixed molar ratio \( \chi_i \) in the bulk solution. The relative value of \( \Gamma_{\text{app},i} \) of BAC surfactants also sheds light on the continuing increase of the concentration of monomeric \( C_{12} \) and the decrease of that of \( C_{14} \) and \( C_{16} \) after mixed micelles start to form as shown in Figs. 6a and 6b. It is confirmed from the results in Fig. 6 that mixed micelles barely form in oil phase at \( C_{\text{tol}} > 2\Gamma_{\text{app}} \) and therefore it is easy to understand most surfactant molecules, including monomeric and micellar forms, exist in aqueous phase (especially at \( C_{\text{tol}} > 2\Gamma_{\text{app}} \)). At

\[
\text{[C710]}
\]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image}
\caption{Equilibrium partitioning properties of mixed BAC surfactants (C12, C14, and C16) at various mixed molar ratios in water (0.171 M NaCl) - oil environments at 40°C: (a) equilibrium concentration of total monomeric surfactants in water, (b) in oil, (c) equilibrium concentration of total surfactants, including monomeric and micellar forms, in water as functions of total initial concentration of surfactants added to water. Symbols: experiment; lines: model prediction. Legend represents various mixed molar ratios of C12/C14/C16. Vertical lines in (a) indicate the values of 2\( \Gamma_{\text{app}} \) for each mixture.}
\end{figure}
mixtures, the partitioning coefficient of each mixed surfactant component is barely affected by mixed molar ratio. The transition point can be interpreted as a characteristic of the hydrophobicity of the surfactant mixture. The higher the transition point, the less hydrophobicity of that mixture, and the less surfactant molecules partitioning into oil phase.

The model application is also extended to water-oil partitioning of other surfactants, as shown in Figs. 8a and 8b for mixed C12OE14 and C12OE30. Figs. 8c and 8d for mixed hexaethoxyethylene nonyl phenyl ether (NPE6) and octaethoxyethylene nonyl phenyl ether (NPE8), and Figs. 8e and 8f for mixed C16 and polyoxyethylene 20 cetyl ether (C16E20) in water-oil environments. As can be seen from Fig. 8a, the predicted and experimental surfactant (monomers) distribution in oil phase (trichloroethylene) for mixed C12OE14 and C12OE30 agree reasonably well. The ethoxylate group (EO) average per molecule in oil phase based on prediction agrees well experimental data whereas reasonbly well. The ethoxylate group (EO) average per molecule in water-oil environments. (c) and (d) are the equilibrium partitioning properties of mixed NPE6 and NPE8 surfactants in water-oil (yclohexane) environments at 25°C: (c) the concentration of monomeric surfactants in the oil phase; (d) molar fraction of surfactants in mixed micelles as a function of C_{oil}. The values of the aqueous cmc and the partitioning coefficients are 2.70 × 10^{-5} M and 4.05 × 10^{-5} M, and 481 and 70 for NPE6 and NPE8, respectively. Mixed ratio: 0.542/0.458. Water/oil volume ratio: 1/1. (e) and (f) are equilibrium partitioning properties of mixed C16 and C16E20 surfactants in water-oil (heptane) environments at 25°C: (e) concentration of monomeric surfactants in 0.03 M NaCl aqueous phase; (f) in oil phase as a function of C_{oil}. The predicted values of the aqueous cmc and the partitioning coefficients from previous work are 3.61 × 10^{-5} M and 2.47 × 10^{-6} M, and 5.32 and 0.66 for C16 and C16E20, respectively. Mixed ratio: 1/1. Water/oil volume ratio: 2/1. Lines: model prediction; symbols: reported data. Reported data in Figs. (a)-(d) are cited from literature. The values of the aqueous cmc and the partitioning coefficients are 2.70 × 10^{-5} M and 4.05 × 10^{-5} M, and 481 and 70 for NPE6 and NPE8, respectively. Mixed ratio: 0.542/0.458. Water/oil volume ratio: 1/1. Lines: model prediction; symbols: reported data. Reported data in Figs. (a)-(d) are cited from literature. The values of the aqueous cmc and the partitioning coefficients are 2.70 × 10^{-5} M and 4.05 × 10^{-5} M, and 481 and 70 for NPE6 and NPE8, respectively. Mixed ratio: 0.542/0.458. Water/oil volume ratio: 1/1. Lines: model prediction; symbols: reported data. Reported data in Figs. (a)-(d) are cited from literature. The values of the aqueous cmc and the partitioning coefficients are 2.70 × 10^{-5} M and 4.05 × 10^{-5} M, and 481 and 70 for NPE6 and NPE8, respectively. Mixed ratio: 0.542/0.458. Water/oil volume ratio: 1/1. Lines: model prediction; symbols: reported data. Reported data in Figs. (a)-(d) are cited from literature. The values of the aqueous cmc and the partitioning coefficients are 2.70 × 10^{-5} M and 4.05 × 10^{-5} M, and 481 and 70 for NPE6 and NPE8, respectively. Mixed ratio: 0.542/0.458. Water/oil volume ratio: 1/1. Lines: model prediction; symbols: reported data. Reported data in Figs. (a)-(d) are cited from literature. The values of the aqueous cmc and the partitioning coefficients are 2.70 × 10^{-5} M and 4.05 × 10^{-5} M, and 481 and 70 for NPE6 and NPE8, respectively. Mixed ratio: 0.542/0.458. Water/oil volume ratio: 1/1. Lines: model prediction; symbols: reported data. Reported data in Figs. (a)-(d) are cited from literature. The values of the aqueous cmc and the partitioning coefficients are 2.70 × 10^{-5} M and 4.05 × 10^{-5} M, and 481 and 70 for NPE6 and NPE8, respectively. Mixed ratio: 0.542/0.458. Water/oil volume ratio: 1/1. Lines: model prediction; symbols: reported data. Reported data in Figs. (a)-(d) are cited from literature. The values of the aqueous cmc and the partitioning coefficients are 2.70 × 10^{-5} M and 4.05 × 10^{-5} M, and 481 and 70 for NPE6 and NPE8, respectively. Mixed ratio: 0.542/0.458. Water/oil volume ratio: 1/1. Lines: model prediction; symbols: reported data. Reported data in Figs. (a)-(d) are cited from literature. The values of the aqueous cmc and the partitioning coefficients are 2.70 × 10^{-5} M and 4.05 × 10^{-5} M, and 481 and 70 for NPE6 and NPE8, respectively. Mixed ratio: 0.542/0.458. Water/oil volume ratio: 1/1. Lines: model prediction; symbols: reported data. Reported data in Figs. (a)-(d) are cited from literature. The values of the aqueous cmc and the partitioning coefficients are 2.70 × 10^{-5} M and 4.05 × 10^{-5} M, and 481 and 70 for NPE6 and NPE8, respectively. Mixed ratio: 0.542/0.458. Water/oil volume ratio: 1/1. Lines: model prediction; symbols: reported data. Reported data in Figs. (a)-(d) are cited from literature. The values of the aqueous cmc and the partitioning coefficients are 2.70 × 10^{-5} M and 4.05 × 10^{-5} M, and 481 and 70 for NPE6 and NPE8, respectively. Mixed ratio: 0.542/0.458. Water/oil volume ratio: 1/1. Lines: model prediction; symbols: reported data. Reported data in Figs. (a)-(d) are cited from literature.
At the partitioning equilibrium, the total monomer concentration \( C_m \) of surfactants in aqueous phase can be calculated using the surfactant distribution model. Considering the equilibrium between monomers in aqueous phase and the adsorbed monomers on the steel surface, the corrosion inhibition efficiency can also be estimated using the modified Langmuir adsorption (MLA) model in Eq. 44. The parameter \( K' \), which is the modified adsorption constant, can be determined by fitting the MLA isotherm.\textsuperscript{34,35} The transferability of \( K' \) is well described in previous work.\textsuperscript{34,35}

\[
\eta \text{ (\%)} = 100 \cdot \theta = \left(1 - \frac{1}{1 + K' \frac{C_m}{\Gamma}}\right) \times 100 \quad \text{[44]}
\]

Potentiodynamic scan curves from the above electrochemical testing system are shown in Fig. 9, in which the corrosion current density \( i_{\text{corr}} \) was determined using Tafel slope method.\textsuperscript{34,35} The corrosion inhibition efficiency \( \eta \text{ (\%)} \) is calculated using the equation below:\textsuperscript{44}

\[
\eta \text{ (\%)} = 100 \times \frac{i_{\text{corr}} - i_{\text{corr}}}{i_{\text{corr}}} \quad \text{[45]}
\]

Table II. Tafel slopes (cathodic \( \beta_c \) and anodic \( \beta_a \)), corrosion rate, polarization resistance, and corrosion inhibition \( \eta \text{ (\%)} \) for X65 electrode in the absence and presence of different concentrations of equal-molar mixed BAC surfactants (C12, C14, and C16) in water (0.599 M NaCl)-toluene-steel electrode environments at 40°C. Volume of water and toluene are 80 mL and 40 mL, respectively.

| Initial concentration \( C_{\text{ml}}, \mu M \) | \( \beta_c \), mV dec\(^{-1} \) | \( |\beta_a| \), mV dec\(^{-1} \) | \( i_{\text{corr}}, \mu A \text{ cm}^{-2} \) | \( \eta \text{, \% }^a \) | \( R_p \text{, ohm} \cdot \text{cm}^2 \) | \( \eta \text{, \% }^b \) |
|-----------------------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 0                                           | 53.4 ± 2.6     | 209 ± 7        | 117 ± 16       | 0              | 158 ± 15       | 0              |
| 0.5                                         | 50.8 ± 2.1     | 215 ± 9        | 111 ± 19       | 5 ± 2          | 160 ± 19       | 2 ± 2          |
| 1                                           | 51.9 ± 2.7     | 208 ± 7        | 107 ± 23       | 9 ± 2          | 169 ± 18       | 7 ± 2          |
| 2.5                                         | 49.6 ± 2.9     | 213 ± 5        | 95 ± 15        | 19 ± 3         | 184 ± 26       | 14 ± 3         |
| 5                                           | 48.3 ± 1.8     | 219 ± 9        | 68 ± 12        | 42 ± 4         | 253 ± 21       | 38 ± 4         |
| 10                                          | 47.2 ± 2.5     | 225 ± 8        | 61 ± 9         | 48 ± 7         | 278 ± 32       | 43 ± 3         |
| 16                                          | 55.4 ± 3.3     | 219 ± 8        | 34 ± 6         | 71 ± 4         | 565 ± 36       | 72 ± 5         |
| 55                                          | 56.1 ± 2.5\(^c\) | 218 ± 8       | 12 ± 4         | 90 ± 3         | 1652 ± 51      | 90 ± 4         |
| 100                                         | 51.2 ± 3.1\(^d\) | 227 ± 10      | 6 ± 2          | 95 ± 4         | 3094 ± 81      | 95 ± 3         |
| 250                                         | 46.9 ± 2.8\(^e\) | 206 ± 7       | 4 ± 1          | 97 ± 3         | 4716 ± 73      | 97 ± 3         |
| 500                                         | 49.3 ± 3.1\(^f\) | 203 ± 12      | 4 ± 2          | 97 ± 2         | 4897 ± 101     | 97 ± 2         |

\(^a\) \eta \text{ (\%)} calculated from potentiodynamic scans.

\(^b\) \eta \text{ (\%)} calculated from LPR.

\(^c\) \eta \text{ (\%)} calculated from polarization resistance as follows:\textsuperscript{34}

\[
\eta \text{ (\%)} = 100 \times \frac{R_\text{p} - R_\text{po}}{R_\text{p}} \quad \text{[47]}
\]

where \( R_\text{po} \) and \( R_p \) are polarization resistances in the absence and presence of surfactants, respectively.

Nyquist curves were plotted based on EIS measurements for the discussed testing system. There are four types of Nyquist plots based on surfactant concentration in aqueous phase: 1) no surfactant; 2) low surfactant concentration, usually lower than the surface aggregation concentration \( \text{sac} \) which is typically the monolayer coverage concentration; 3) surfactant concentration around the monolayer coverage concentration; 4) surfactant concentration greater than the monolayer coverage concentration, including the micelle formation concentration. Examples of these four types of Nyquist plots are given in Fig. 10.
It was found that with lower surfactant concentration, typically lower than the monolayer coverage concentration, the impedance plot features a capacitive semicircle at high frequency and an inductive semicircle at low frequency. The increase in the diameter of capacitive semicircle with the increase in the surfactant concentration is in good agreement with the results of LPR and PDS measurements. The increase in the diameter of capacitive semicircle at low frequency represents the formation of a porous surfactant film. When surfactant concentration is higher than the monolayer coverage concentration, the 2nd semicircle is clearly seen and indicates the coverage of bilayers/multilayers/semi-micelles on the electrode surface.

Based on the EIS measurements, four different types of electrochemical equivalent circuits, which are given in Fig. 11, were used to fit the measured electrochemical behavior of the ternary mixture of BAC surfactant systems. The different circuits demonstrate the mechanistic change in the corrosion process, as indicated by the shapes of Nyquist plots. In Fig. 11, Rs is solution resistance, Rct is charge transfer resistance for evaluation of corrosion inhibition efficiency of surfactants, R1 is inductor resistance, R1 and R2 are the resistances of the formed monolayers and bilayers/multilayers/semi-micelles respectively, Ycpe1 and Ycpe2 are the pseudo capacitances of cpe1 (constant phase element 1) and cpe2 corresponding to monolayers and bilayers/multilayers/semi-micelles respectively, L is the inductance of an inductor, and Ycpedl is the pseudo capacitance of cpdl which represents the electric double layer. Zas and Zm2 represent the impedance of porous bounded Warburg elements W1 and W2, which are characterized by parameters W1 and P1, and W2 and P2, respectively. The fitted curves of equivalent circuits are presented in Figs. 10 and the values of fitted impedance parameters are summarized in Table III.

The comparison of predicted and experimental corrosion current density as a function of time of equal-molar mixed BAC surfactants (C12, C14, and C16) at C_M = 1.50 × 10⁻⁴ M with water/oil volume fraction of 2.

![Figure 11. Equivalent circuits for Nyquist plots of EIS measurements for X65 electrode in the absence and presence of different concentrations of equal-molar mixed BAC surfactants (C12, C14, and C16) in water (0.599 M NaCl)-toluene-steel electrode environments at 40°C: (a) no surfactant; (b) low surfactant concentration, usually lower than the monolayer coverage concentration; (c) surfactant concentration around the monolayer coverage concentration; (d) surfactant concentration greater than the monolayer coverage concentration.](image-url)

### Table III. Equivalent circuit parameters of EIS plots for X65 electrode in the absence and presence of different concentrations of equal-molar mixed BAC surfactants (C12, C14, and C16) in water (0.599 M NaCl)-toluene-steel electrode environments at 40°C. C (μM), R (Ω·cm²), W (10⁻⁶·Ω⁻¹·s⁰·cm⁻²), Y (10⁻⁶·Ω⁻¹·s⁰·cm⁻²), L (H·cm⁻²), η (%). Water/oil volume ratio is 2.

| C  | Blank | 0.5 | 1   | 2.5 | 5   | 10  | 16  | 55  | 100 | 250 | 500 |
|----|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Rₐ | 8.1   | 7.9 | 6.4 | 8.2 | 8.9 | 9.1 | 9.0 | 9.6 | 8.1 | 7.2 | 8.8 |
| P₂ | ----  | ----| ----| ----| ----| ----| ----| ----| 4.5 | 5.3 | 6.4 |
| W₂ | ----  | ----| ----| ----| ----| ----| ----| ----| 7236| 6941| 5356|
| Ycpe₂| ---- | ----| ----| ----| ----| ----| ----| ----| 7923| 7105| 6709|
| ncpe₂| ---- | ----| ----| ----| ----| ----| ----| ----| 1   | 1   | 1   |
| R₁ | ----  | ----| ----| ----| ----| ----| ----| ----| 11.4| 15.2| 18.7|
| P₁ | ----  | ----| ----| ----| ----| ----| ----| ----| 1.50| 55.9| 77.2|
| W₁ | ----  | ----| ----| ----| ----| ----| ----| ----| 2640| 3542| 2840|
| Ycpe₁| ----| 334 | 291 | 257 | 246 | 228 | 197 | 1045| 1562| 989 | 742 |
| ncpe₁| ----| 0.86| 0.83| 0.79| 0.79| 0.84| 0.84| 0.82| 0.92| 0.95| 0.91|
| R₁ | ----  | 4.4 | 7.6 | 13.6| 21.8| 19.5| 16.3| 21.9| 8.5 | 21.2| 31.4|
| L  | 24201 | 29758| 62321| 102085| 121506| 142038| 147296| ----| ----| ----| ----|
| Rₙ | 319   | 1278| 1396| 1766| 1971| 2012| 2132| ----| ----| ----| ----|
| Ycpeₙ| 919  | 296 | 239 | 223 | 198 | 179 | 156 | 176 | 152 | 75  | 66  |
| ncpeₙ| 0.81 | 0.86| 0.86| 0.82| 0.83| 0.80| 0.86| 0.86| 0.89| 0.88| 0.85|
| Rₙ ± 11%*| 136 | 143 | 155 | 179 | 220 | 283 | 504 | 1511| 2267| 2720| 2894|
| η   | 0    | 5 ± 2| 12 ± 2| 24 ± 3| 38 ± 2| 52 ± 6| 73 ± 4| 91 ± 3| 94 ± 4| 95 ± 3| 96 ± 3|

*average value of at least three measurements.
is no longer applicable and the predicted corrosion inhibition efficiency agrees with experimental data and the calculated data based on transfer free energy method, and a group contribution method. The experimental data and the calculated data based on transfer free energy method, and a group contribution method agree very well.

The predicted corrosion inhibition efficiency based on the modified quantitative structure activity relation (MQSAR) for mixed BAC surfactants which is cited from reported work is also presented in Fig. 9b and is comparable to the experimental data and MLA prediction. The associated results are also summarized in Table IV.

Table IV. Equilibrium concentrations of total monomers in aqueous phase at partitioning equilibrium and the corrosion inhibition efficiency from measurements and model prediction for equal-molar mixed BAC surfactants (C12, C14, and C16) in water (0.599 M NaCl)-toluene-steel electrode environments at 40 °C. Volume of water and toluene are 80 mL and 40 mL, respectively.

| Initial concentration C_{tol}, μM | Aqueous monomer concentration C_{aq}, μM | η, % | LPR | PDS | EIS | MLA Prediction |
|----------------------------------|----------------------------------------|------|-----|-----|-----|----------------|
| 0.5                              | 0.28 ± 0.02                            | 2 ± 2| 5 ± 2| 5 ± 2| 6   |
| 1                                | 0.55 ± 0.05                            | 7 ± 2| 9 ± 2| 12  |
| 2.5                              | 1.38 ± 0.05                            | 14 ± 3| 19 ± 3| 24 ± 3| 26  |
| 5                                | 2.76 ± 0.06                            | 38 ± 4| 42 ± 4| 38 ± 2| 41  |
| 10                               | 5.53 ± 0.2                             | 43 ± 3| 48 ± 5| 52 ± 4| 58  |
| 15                               | 8.85 ± 0.2                             | 72 ± 5| 71 ± 4| 73 ± 4| 69  |
| 55                               | 27.6 ± 0.6                             | 90 ± 4| 90 ± 3| 91 ± 3| 88  |
| 100                              | 55.3 ± 1.2                             | 95 ± 3| 95 ± 4| 94 ± 4| 93  |
| 250                              | 80.6 ± 2.1                             | 97 ± 3| 97 ± 3| 95 ± 3| 93  |
| 500                              | 102 ± 3.8                              | 97 ± 2| 97 ± 2| 96 ± 3| 93  |

Conclusions

1. One water-oil surfactant distribution model for the evaluation of the water-oil partitioning of surfactant is proposed and validated. This model is applicable over a wide total surfactant concentration range, including the aqueous cmc, the oil cmc, and the apparent cmc. The surfactant distribution model, which is a combination of a surfactant partitioning sub-model, a partitioning coefficient calculation method, and the developed cmc prediction sub-model based on previous work, provides one potential tool to evaluate the partitioning of surfactant mixture (either homologous or non-homologous) in water-oil environments. The model predicted data and the experimental/reported data of surfactant distribution in water-oil environments agree very well.

2. For pure surfactant partitioning in water-oil environments, the equilibrium concentration in the aqueous/oil phase of surfactant increases linearly with the initial concentration added to the system up to around the aqueous cmc. Above the aqueous cmc, surfactant starts to accumulate and form micelles in either the aqueous phase, the oil phase, or both phases. It is confirmed that C_{12} and C_{14} form micelles in the aqueous phase and C_{16} primarily in the oil phase.

3. The temperature effect on the water-oil partitioning of C_{16} was also evaluated. K_{16} increases with the increasing temperature. The calculated transfer free energy of head group is validated in the calculation of the partitioning coefficients of BAC surfactants under various partitioning conditions.

4. Different methods to calculate partitioning coefficient are introduced, which includes an experimental measurement, a transfer free energy method, and a group contribution method. The experimental data and the calculated data based on transfer free energy agree very well.

5. The mixed micelles start to form only after the transition point (the apparent cmc of the mixture) is reached in water-oil partitioning of the mixed surfactants. The partitioning coefficient of each mixed surfactant component is barely affected by the bulk mixed molar ratio. The apparent cmc of surfactant mixture can be interpreted as a characteristic of hydrophobicity/hydrophilicity of that mixture. The higher the apparent cmc, the less hydrophobicity of that mixture, and the less surfactant molecules partitioning into the oil phase.

Figure 12. (a) Comparison of the predicted and the experimental corrosion current density as a function of time for the equal-molar mixed BAC surfactants (C12, C14, and C16) at C_{tol} = 1.50 × 10^{-3} M with water/oil volume ratio of 2:1. The NaCl concentration in aqueous phase is 0.599 M. (b) Comparison of the predicted inhibition efficiency (from MLA and MQSAR) and the experimental inhibition efficiency on steel corrosion of the mixed surfactant system. Symbols: experiment; curves: prediction. The vertical line indicates the transition point at C_{tol} = 1.5Γ_{app}, where micelles form in water-oil environments. K^\ast = 13.74 in MLA model for mixed BAC surfactants. The quantum descriptors of the mixed BAC surfactants are the molar-based average values of the reported quantum descriptors of the pure BAC surfactants. The regression coefficients in MQSAR are reported values.35
6. The higher the apparent cmc of surfactant ‘i’ in water-oil environments, the higher the hydrophobicity, and thus the higher the mixed molar fraction $\chi_i$ of surfactant ‘i’ in micelles at the initiation of micelle formation. The molar fraction $\chi_i$ eventually approaches the initial bulk mixed molar ratio $\chi$ as the total concentration increases. It is applicable to both one-phase (water) and two-phase (water and oil) environments. The apparent cmc of pure surfactant can also explain the selective partitioning of mixed surfactants.

7. The effect of partitioning on corrosion inhibition efficiency of mixed surfactants was initially evaluated by the modified Langmuir adsorption and by the electrochemical measurements. The corrosion inhibition efficiency from the model prediction and from the experimental measurements is comparable.

Acknowledgments

The presented research is supported by a grant from BP. CHPC at the University of Utah is acknowledged for providing computational resources. Jim Muller and George Russell were acknowledged for the testing of partitioning samples using mass spectrometry. Thank Dr. D. I. Fletcher for discussions on partitioning cell design.

List of Symbols

The following symbols represent the equilibrium condition in a water-oil two phase environment unless a special condition is specified.

cpedl  electric double layer.  
cpe1  constant phase element 1 corresponding to surface monolayer.  
cpe2  constant phase element 2 corresponding to bilayers/multilayers/semi-micelles.  
$\tilde{C}$  overall average concentration of total surfactants in water-oil environment.  
$C_i^o$  overall concentration of total surfactant ‘i’ in oil phase.  
$C_i^w$  overall concentration of total surfactant ‘i’ in water phase.  
$C_m$  overall concentration of total monomers in mixed water-oil environment.  
$C_{mi}$  overall concentration of monomeric surfactant ‘i’ in water-oil environment at saturation.  
$C_{mi}^o$  concentration of monomeric surfactant ‘i’ in oil phase.  
$C_{mi}^w$  concentration of monomeric surfactant ‘i’ in water phase.  
$C_w$  molar concentration of water.  
$C_m$  molar concentration of oil.  
$C_w^o$  concentration of total monomers in water phase.  
$C_m^o$  concentration of total monomers in oil phase.  
$C_i^o$  concentration of total surfactants in oil phase.  
$C_i^{\text{eq}}$  initial concentration (not at equilibrium) of total surfactants in water phase.  
$C_i^w$  concentration of total surfactants in water phase.  
$f_i$  activity coefficient of surfactant ‘i’ in micelles.  
$f_{i,\text{corr}}$  corrosion current density without surfactants in solution.  
$I_{\text{corr}}$  corrosion current density with surfactants in solution.  
$I$  ionic strength of solution.  
$k$  Boltzmann constant.  
$k_{\text{S}}$  Setchenov coefficient per CH2 group.  
$L_i$  partitioning coefficient of surfactant ‘i’.  
$L_{\text{app}}$  apparent partitioning coefficient of mixed surfactants.  
$L_x$  the inductance of an inductor.  
$L_i$  hydrocarbon chain length of surfactant ‘i’, which means the C atom number in chain.  
$R_C$  charge transfer resistance.  
$R_x$  inductor resistance.  
$R_p$  polarization resistance in presence of surfactants.  
$R_{po}$  polarization resistance in the absence of surfactants.  
$R_o$  solution resistance.  
$R_1$  resistance of the formed monolayers on electrode surface.  
$R_2$  resistance of the formed bilayers/multilayers/semi-micelles on electrode surface.  
$T$  temperature.  
$V_n$  volume of oil phase.  
$V_w$  volume of water phase.  
$w_1$  porous bounded Warburg element 1 corresponding to surfactant monolayer and characterized by parameters $W_1$ and $P_1$.  
$w_2$  porous bounded Warburg element 2 corresponding to bilayers/multilayers/semi-micelles and characterized by parameters $W_2$ and $P_2$.  
$\chi_i$  molar fraction of surfactant ‘i’ in the total amount of mixed surfactants in water-oil environment.  
$X_i^w$  molar fraction of surfactant ‘i’ in total amount of molecules in water phase.  
$X_i^o$  molar fraction of surfactant ‘i’ in total amount of molecules in oil phase.  
$X_i^\text{app}$  molar fraction of counter ‘j’ in total amount of molecules in water phase.  
$Y_{\text{cpdcl}}$  pseudo capacitance of cpedcl.  
$Y_{\text{cpe1}}$  pseudo capacitance of cpe1.  
$Y_{\text{cpe2}}$  pseudo capacitance of cpe2.  
$Z_m$  impedance of w1.  
$Z_{w1}$  impedance of w2.  
$\alpha_i$  molar fraction of surfactant ‘i’ in mixed micelles.  
$\beta_o$  anodic Tafel slope.  
$\gamma_i^o$  anodic Tafel slope.  
$\gamma_i^w$  cathodic Tafel slope.  
$\gamma_{\text{mi}}$  activity coefficient of monomeric surfactant ‘i’ in water phase.  
$\gamma_{\text{mi}}^o$  activity coefficient of monomeric surfactant ‘i’ in oil phase.  
$\gamma_{\text{mi}}^w$  activity coefficient of counterion ‘j’ in water phase.  
$\gamma_{\text{mi}}^{\text{elec}}$  functional headgroup activity coefficient of surfactant ‘i’ in water phase.  
$\mu_i$  hydrocarbon chain tail activity coefficient of surfactant ‘i’ in water phase.  
$\mu_{\text{mi}}$  binding coefficient to micelles of counterion ‘j’.  
$\delta_i$  surface coverage.  
$\Gamma_{\text{app}}$  the average concentration in water-oil environments of mixed surfactants at which mixed micelles start to form.  
$\Gamma_{\text{app},i}$  the average concentration in water-oil environments of surfactant ‘i’ at which micelles start to form.  
$\Gamma_i^o$  oil cmc value of surfactant ‘i’.  
$\Gamma_i^w$  aqueous cmc value of surfactant ‘i’.  
$\theta$  aqueous cmc value of mixed surfactants.  
$\mu_i^o$  chemical potential of monomeric surfactant ‘i’ in water phase.  
$\mu_i^w$  chemical potential of surfactant ‘i’ in mixed micelles.  
$\mu_i^{\text{elec}}$  chemical potential of monomeric surfactant ‘i’ in oil/organic phase.  
$\mu_{\text{mi}}^o$  chemical potential of surfactant ‘i’ in pure micelles.  
$\mu_{\text{mi}}^{\text{elec}}$  standard chemical potential of monomeric surfactant ‘i’ in organic phase.  
$\mu_{\text{mi}}^{\text{pot}}$  chemical potential of counterion ‘j’ in water phase.  
$\mu_{\text{mi}}^{\text{pot}}$  chemical potential of counterion ‘j’ in water phase.  
$\mu_{\text{mi}}^{\text{pot}}$  chemical potential of counterion ‘j’ in water phase.  
$\Delta H_i^o$  enthalpy change of transfer of surfactant ‘i’ from aqueous phase to organic phase.  
$\Delta S_i^o$  entropy change of transfer of surfactant ‘i’ from aqueous phase to organic phase.  
$\Delta \mu_{\text{act}}^o$  standard free energy contribution from the activity of surfactant and counterion.  
$\Delta \mu_{\text{elec}}^o$  standard free energy contribution from electrostatic interaction.  
$\Delta \mu_{\text{pot}}^o$  standard free energy contribution from entropy gain associated with headgroup-counterion mixing.
\( \Delta G_{\text{mix}} \) standard free energy contribution from formation of micellar core-water interface.

\( \Delta G_{\text{mic}} \) standard micellization free energy per surfactant molecule with consideration of solution composition of surfactant and with incorporation of surfactant activity and counterion activity. This is the total free energy that is minimized in the model.

\( \Delta G_{\text{pack}} \) standard free energy contribution from hydrocarbon tail packing in the micelle.

\( \Delta G_{\text{ct}} \) standard free energy contribution from surfactant head-group steric interaction.

\( \Delta G_{\text{tr}} \) standard free energy contributions from hydrocarbon transfer from water into organic phase.

\( \Delta G_{\text{tri}} \) standard free energy change of transfer of surfactant ‘i’ from aqueous phase to organic phase.

\( \Delta G_{\text{triu}} \) standard free energy change of transfer of surfactant ‘i’ from aqueous phase to organic phase.

\( \Delta G_{\text{trui}} \) standard free energy change of transfer of head group of surfactant ‘i’ from salt water to organic phase.

\( \Delta G_{\text{trmi}} \) standard free energy change of transfer of hydrocarbon chain of surfactant ‘i’ from salt water to organic phase.

\( \Delta G_{\text{trsi}} \) standard free energy change of transfer of hydrocarbon chain of surfactant ‘i’ from salt water to pure water.

\( \Delta G_{\text{trwi}} \) standard free energy change of transfer of hydrocarbon chain of surfactant ‘i’ from pure water to organic phase.

\( \Delta G_{\text{trwi}} \) standard free energy change of transfer of methyl group from pure water to organic phase.

\( \Delta G_{\text{trch2}} \) standard free energy change of transfer of methylene group from pure water to organic phase.

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