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Colloids and Surfaces A: Physicochemical and Engineering Aspects

Experimental investigation and modeling of the performance of pure and mixed surfactant inhibitors: Micellization and corrosion inhibition

Yakun Zhu*, Michael L. Free

Department of Metallurgical Engineering, University of Utah, 135 S 1460 E, Rm 412, Salt Lake City, UT 84112, USA

HIGHLIGHTS

- Surfactant adsorption and associated corrosion inhibition is highly affected by aggregation.
- One critical micelle concentration model is developed to evaluate aggregation in salt solution.
- The critical micelle concentration model is combined with modified Langmuir adsorption and modified quantitative structure activity relation.
- The predicted corrosion inhibition from the above model combination agrees well with experimental data.

GRAPHICAL ABSTRACT
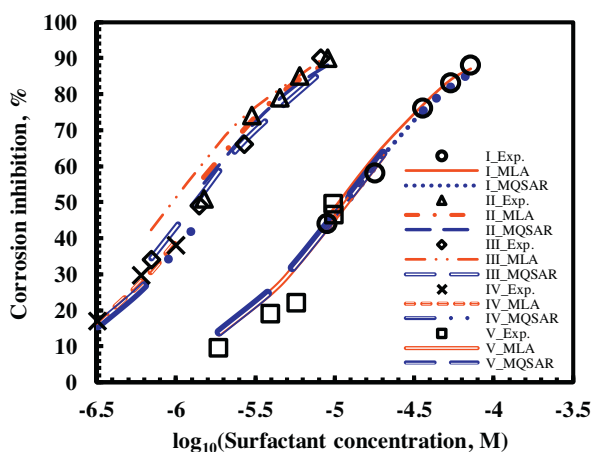
ABSTRACT

Surfactants have been widely used as inhibitors for metal corrosion inhibition by their adsorption on metal surface to act as a protective film. The adsorption, however, is highly affected by surfactant micellization which needs a systemic study. An improved critical micelle concentration (cmc) prediction model is developed and validated to study micellization of various pure and mixed surfactants in aqueous solution containing salts (0–3 M). The effects of counterion and coion specificity on aggregation properties are successfully evaluated. The predicted aggregation properties, including critical micelle concentration (cmc), micelle shape, micelle aggregation number, and sphere-to-rod transition, agree well with experimental data. The cmc model, in combination with improved adsorption evaluation approach, the modified Langmuir adsorption and the modified quantitative structure activity relation, provides a method to evaluate the effects of micellization on surfactant adsorption and associated corrosion inhibition performance.

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1. Introduction

As an important component of the economy, the oil and gas industry has received considerable attention from researchers because oil mining and transportation have become increasingly

* Corresponding author. Fax: +1 801 581 4937.
E-mail address: yakun.zhu@utah.edu (Y. Zhu).

expensive due to equipment (metallic pipelines) damage caused by corrosion, especially CO_2 corrosion [1–5]. The concerns have led to great interest in industry and academia to control corrosion of metallic pipelines in various oilfields around the world. Among the existing corrosion control methods, surfactant inhibitors have widely been used for corrosion inhibition of pipelines in water-oil-steel pipe (WOS) environments [1,2]. Particularly, surfactant mixtures are well known due to the superior physicochemical properties and capabilities in efficient solubilization, adsorption, and suspension etc. [1,2,6–8]. More surface-active and expensive surfactants are often mixed with less surface-active and cheaper surfactants to reduce cost [1,2,9]. The use of surfactant inhibitors for corrosion inhibition is based on the fact that surfactant molecules adsorb on and cover metal surface and slow down one or more electrochemical reactions associated with metal dissolution and thus inhibit corrosion [1,2,9,10]. The adsorption process, however, is highly affected by the other main processes upon the addition of surfactants to WOS environments, such as micellization and water/oil partitioning [10] which tend to deplete monomeric surfactants available for the adsorption and effective coverage on metal surface. Therefore, it is necessary to understand micellization process for a systematic evaluation of corrosion inhibition using various pure and mixed surfactants in WOS environments [1,2,10].

More recently, it has been reported that the cmc has been successfully coupled with mechanistic evaluation approaches which are modified Langmuir adsorption (MLA) and modified quantitative structure activity relation (MQSAR) to predict corrosion inhibition efficiency η (%) [1,2,5,9]. The MLA and MQSAR are briefly introduced below. Details of derivation, validation, and application have been reported elsewhere [1,2,5,9].

MLA model:

$$\eta\,(\%) = \left(1 - \frac{1}{1 + K' \frac{C}{\Gamma^w}} \right) \times 100 \tag{1}$$

MQSAR model:

$$\eta\,(\%) = \frac{\left(\vec{A}' \cdot \vec{Q} + \vec{B}' \right) C}{\Gamma^w + \left(\vec{A}' \cdot \vec{Q} + \vec{B}' \right) C} \times 100 \tag{2}$$

where C is the concentration of surfactants in the bulk solution, Γ^w is the aqueous cmc of surfactant mixture, K' is equal to the adsorption constant K_{ad} multiplied by Γ^w, and η is corrosion inhibition efficiency. $\vec{A}'$ is a modified vector of regression coefficients, and $\vec{B}'$ is a modified regression constant. $\vec{Q}$ is a vector of quantum chemical descriptors for a particular surfactant. For surfactant mixtures the quantum chemical descriptors are weight-based average values. Note that for pure surfactant, Γ^w is replaced by the aqueous cmc of pure surfactant i, Γ_i^w.

Therefore, the present work is thus focused on the micellization properties of surfactants in salt solutions. One of the challenges in the study of micellization comes from the effects of specific ions and added salts. Different counterions usually present different effects on the critical micelle concentration (cmc), micelle shape, micelle growth, micelle size and distribution, mixed micelle composition (for mixed surfactants), and phase separation [11–18]. It is reported that the counterion effect on the aggregation properties of cationic surfactants is usually stronger than that of anionic surfactants [15,16]. In addition, the cmc depression due to counterion effect usually follows the Hofmeister series: $OH^- < F^- < Cl^- < Br^- < NO_3^- < ClO_3^- < I^- <$ benzoate$^- <$ salicylate$^-$ for cationic surfactants; and $Li^+ < Na^+ < K^+ < C_s^+$ for anionic surfactants [15,16]. The specific counterion effects on micelle size and sphere-to-rod transition is usually in the same order as shown previously for cmc [16]. The counterion binding mechanism is not clear and has been a controversial issue [19].

At low salt concentration the coion effect on cmc, aggregation number, and sphere-to-rod transition is negligible [20,21]. However, as salt concentration increases the coion effect becomes increasingly noticeable [20,21]. Particularly at relatively high salt concentration the coion effect on aggregation properties becomes dramatic as discussed in the text below.

The authors are not aware of a completely established theory or model to adequately describe the effects of ion specificity and binding mechanism on surfactant aggregation properties despite extensive progress in theoretical and experimental work.

In the approach proposed by Nagarajan and Ruckenstein [22] based on the work from Evans and Ninham [23], Nagarajan [22] successfully incorporates a parameter which is the distance between the surface of a hydrophobic/micellar core (the micellar core is the micelle with hydrophobic chain and without headgroup) and the center of counterions. This parameter, according to Nagarajan [23], is dependent on headgroup size, hydrated counterion size, and the distance from the counterion to the charge of ionic surfactant. However, Nagarajan does not provide more details about these dependencies.

The molecular thermodynamic theory (MTT) [12,24–26] provides a great step in progress toward the understanding and modeling of counterion specificity on ionic surfactant micellization. In the theory, the counterion is assumed to bind to the micelle surface in terms of fractional coverage between 0 and 1, and it affects the magnitude of various free energy contributions to the micellization process. The predicted cmc as well as some other properties such as aggregation number and mixed micelle composition are in relatively good agreement with experiment. However, the theory does not clarify the specificity of headgroup–counterion pair interactions.

More recently Moreira and Firoozabadi (MF) [20] improved to some extent the existing MTT [12,22,24–27] by the introduction of solvent-shared specific counterion–headgroup pairs. However, the MF model only applies to the spherical and globular micelles in a very narrow range of added salt concentration and does not take into account the sphere-to-rod transition and growth of micelles to long cylinders.

Koroleva and Victorov (KV) [28] developed a model that introduces the specific headgroup–counterion pair in which a geometric parameter, called the distance of the closest approach of the ion to the core, is added to take into account hydration effects. Moreover, they adopted a modified Poisson–Boltzmann equation (PB) [29] that incorporates the dispersion interactions between ions and micelles to differentiate the polarizability of different ions, which has also been considered by recently reported work [30]. The predicted cmc, aggregation number, and sphere-to-rod transition are in reasonably good agreement with experiment. However, the incorporation of dispersion interaction between counterion and micelle in the modified PB equation does not adequately reflect the effect of counterion specificity on cmc [20].

In the present work, an alternative cmc model is developed and validated which incorporates the surfactant activity, counterion activity, headgroup–counterion pairing, and ion effects on surfactant aggregation. The activity coefficient of ions is evaluated using Pitzer's method [31,32] or Davies [33] equation depending on the salt concentration. The activity coefficient of surfactants is evaluated from the Setchenov equation [34]. The effect of coion is evaluated from salt-dependent factors, including the Setchenov coefficient k_s [28,34], the dielectric decrement of salt δ_s [25], and the correlation between the change of surface tension and the change of salt concentration in aqueous solution, $d\sigma_0/dC_s$ (σ_0 is surface tension and C_s is salt concentration) [25] (Symbol definition can be found in Appendix A).

The developed cmc model was further incorporated into the MLA and the MQSAR models for the prediction of the effects of