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Interfacial Equation of State for Ionized Surfactants at Oil/Water Interfaces

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ABSTRACT

A new mathematical approach has been developed for describing the interfacial behaviour of oil/water interfaces in the presence of ionic surfactants. The approach relies on the ideal behaviour of ionized surfactants at oil/water interfaces, which is previously demonstrated by Lucassen-Rynders (J. Phys. Chem., 70 (1966) 1777-1785). The new derived equation simply relates the interfacial tension to the surfactant molecular size and the *cmc* value of the surfactant in the aqueous phase. The predicted values are in a reasonable agreement with the measured experimental data. Formation of complex multi-layers is considered and the related development is performed. It is shown that, assuming a multi-layer interface, the proposed model gives an area per surfactant molecule similar to the values obtained by techniques such as neutron reflectivity (NR), while a monolayer assumption yields about half the value, reported by the NR method. The discussion describes the impact of dissolved oil and ionic components on the interfacial tension of the ionized surfactants at oil/water interfaces.

Introduction

Physical, chemical and electrical properties of systems at fluid-fluid interfaces are significantly different from those in the bulk. There are many systems in which interfacial properties make a negligible contribution to the overall behaviour of the system. In such cases, the total mass attributed to the interfaces is very small and negligible in comparison with the masses localized in bulk solutions. There are also many systems and many industrial processes in which the interfacial properties are dominant and governing factors. Examples are dispersions or colloidal solutions, paint technology, detergents, emulsions, food science, ore floatation, oil recovery from hydrocarbon reservoirs, etc. All of these important processes are profoundly reliant upon surfactant properties and their usage.¹ These compounds are used as surface modifiers and they can dramatically change the interfacial properties even in a very small dosage.

The impact of surfactant molecules on the interfacial tension is regularly described by an interfacial equation of state. An interfacial equation of state is a relationship between surface pressure or $\sigma_0 - \sigma$ and $c(s)$. Here, σ_0 is the interfacial tension of the system without surfactant, σ is the interfacial tension after addition of the surfactant into the system and $c(s)$ is the surfactant surface concentration. The surface concentration is generally related to the surfactant bulk phase concentration using an equilibrium adsorption constant. The semi-empirical equation of Szyszkowski and the well-known Langmuir model are two examples of the kind.² None of the available surface equations of state can be used to predict the interfacial tension between single surfactant solutions. In fact they are more of a curve-fitting procedure than a prediction.

Currently, there are two well-known methods^{3,4} available for prediction of oil/water interfacial tension in the presence of surfactant mixtures. Both models are rigorous and reliably predict the interfacial tensions between oil and mixed surfactant solutions without recourse to the experimental data from the system, having less or no predictive value for individual surfactant solutions.

The Mulqueen-Blankschtein's model⁴ is based on the well-known approach of considering the interface as an insoluble gaseous film. According to this model, an equation of state representing

the relation of the surface pressure with surface molar area and temperature exists and surface pressure (or the interfacial tension) can be simply calculated knowing the surface molar area. The surface molar area can be calculated from equalizing the chemical potential of the surfactant compound at the film and in the bulk provided that the difference of the standard chemical potential at the film and the standard chemical potential in the bulk is known. This parameter can be found making use of a single interfacial tension measurement. For surfactants with considerable partitioning between the oil and aqueous phase, the partition coefficient also must be known. The model suggests the calculation of this parameter from two interfacial tension measurements. At the very most, therefore, two experimental data for each surfactant molecule are required. Once the unknown parameters for each surfactant molecule are found they can be used to predict the interfacial tension of the surfactant mixtures without requiring any other experimental information and without conducting any additional measurement. The method requires some molecular parameters that are not easily obtainable for many surfactants and involves a demanding computational procedure solving a set of $n + 1$ equations for systems containing n surfactants.

The second approach,^{3, 5-7} is mainly developed by Miller's research group at The Max Planck Institute of Colloids and Interfaces, Germany. According to this method, just one simple equation suffices for prediction of liquid-fluid interfacial tension in presence of surfactant mixtures. The method is simple, rigorous and reliably predictive for mixed surfactant solutions but has no predictive value for individual surfactant systems. In fact, this method requires the adsorption isotherm or the interfacial tension of single surfactant systems as input data. The predictive power of the model for mixed surfactant solutions is reliably demonstrated, assuming no additional interaction parameter between the different components.

In the next section, a simple interfacial equation of state is presented for ionized surfactants at oil-water interfaces. The equation relies on the rule obtained by Lucassen-Reynders⁸ about the ideal state of the ionized surfactant molecules at oil/water interfaces. As will be seen, the new equation can be reasonably used for prediction of oil/water interfacial tension in presence of an ionized surfactant. The paper also presents a discussion on the impact of formation of complex

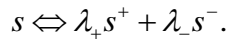
multi-layers at the interface of dissolved organic compounds and of dissolved salt on the interfacial properties of ionic surfactants at oil/water interfaces.

Theory

From the classical thermodynamic viewpoints, it is easy to show that:⁹

$$\sigma = \frac{RT}{a_i} \ln \left(\frac{X_i^{\alpha\beta} \gamma_i^{\alpha\beta}}{X_i^\alpha \gamma_i^\alpha} \right) \quad (1)$$

where, R is universal gas constant, X_i is mole fraction, γ_i is activity coefficient, a_i is partial molar surface area of i th component, and σ is the interfacial tension. The superscript $\alpha\beta$ denotes the interface between bulk phases α and β . The above equation can be written for all of the non-ionic molecules. For ionic components, the equation changes considering the dissociation of the molecules. As a general example, we may consider the ionization of an ionic surfactant which dissociates into λ_+ cations each with a charge z_+ and λ_- anions of charge z_- , as;



Considering the above ionization reaction, the final equation for interfacial tension as a function of the mole fraction of surfactant in bulk and at the interface is:

$$\sigma = \frac{RT}{(\lambda_+ + \lambda_-) a_{s\pm}} \ln \left(\frac{(X_{s+}^{\alpha\beta})^{\lambda_+} (X_{s-}^{\alpha\beta})^{\lambda_-} (\gamma_{s+}^{\alpha\beta})^{\lambda_+} (\gamma_{s-}^{\alpha\beta})^{\lambda_-}}{(X_{s+}^\alpha)^{\lambda_+} (X_{s-}^\alpha)^{\lambda_-} (\gamma_{s+}^\alpha)^{\lambda_+} (\gamma_{s-}^\alpha)^{\lambda_-}} \right) \quad (2)$$

Since the system is dilute, the molar fractions of the ion and counter-ion can be reasonably assumed as equal with that of the surfactant molecules, times the corresponding λ -value in that $X_{s\pm} = \lambda_\pm X_s$. Therefore,

$$\sigma = \frac{RT}{(\lambda_+ + \lambda_-) a_{s\pm}} \ln \left(\frac{(X_s^{\alpha\beta})^{\lambda_+ + \lambda_-} (\gamma_{s\pm}^{\alpha\beta})^{\lambda_+ + \lambda_-}}{(X_s^\alpha)^{\lambda_+ + \lambda_-} (\gamma_{s\pm}^\alpha)^{\lambda_+ + \lambda_-}} \right) \quad (3)$$

where a_s is the partial molar surface area of the surfactant. The above equation can be more simplified considering the work of Lucassen-Reynders⁸ about the activity coefficients of surfactants at oil/water interfaces. It is shown by Lucassen-Reynders, and supported later by other researchers,¹⁰⁻¹³ that ionized surfactants form ideal surfaces (i.e. $\gamma_{s\pm}^{\alpha\beta}=1$) over the entire range of surface pressure. Thus, the mole fraction of an ionic surfactant at the interface can be expressed as;

$$X_s^{\alpha\beta} = (X_s^{\alpha} \gamma_{s\pm}^{\alpha}) \exp\left(\frac{a_{s\pm}}{RT} \sigma\right). \quad (4)$$

It has also been shown recently⁹ that the activity coefficient of a non-surfactant molecule at the oil/water interface is equal to the geometrical mean of that component's activity coefficients in the oil and water bulk phases. Employing this rule, remembering that $\gamma_i^{\alpha} X_i^{\alpha} = \gamma_i^{\beta} X_i^{\beta}$ and using Equation 1, results in the following equation for the mole fraction of non-surfactant molecules at the interface:

$$X_i^{\alpha\beta} = \sqrt{(X_i^{\alpha} X_i^{\beta})} \exp\left(\frac{a_i}{RT} \sigma\right). \quad (5)$$

Summation of mole fractions at the interface must equal unity. Thus:

$$X_s^{\alpha\beta} + \sum_i X_i^{\alpha\beta} = 1 \quad (6)$$

and therefore, from equations 4 and 5,

$$\left(X_s^{\alpha} \gamma_{s\pm}^{\alpha}\right) \exp\left(\frac{a_{s\pm}}{RT} \sigma\right) + \sum_i \left(\sqrt{(X_i^{\alpha} X_i^{\beta})} \exp\left(\frac{a_i}{RT} \sigma\right)\right) = 1 \quad (7)$$

Considering the equality of partial molar surface areas, discussed elsewhere,^{14, 15} Equation 7 can be further simplified to:

$$\exp\left(-\frac{a}{RT} \sigma\right) = (X_s^{\alpha} \gamma_{s\pm}^{\alpha}) + \sum_i \left(\sqrt{(X_i^{\alpha} X_i^{\beta})}\right) \quad (8)$$

where a is the molar surface area of the system. When there is no surfactant in the system, the equation reduces to:

$$\exp\left(-\frac{a}{RT}\sigma_0\right) = \sum_i \left(\sqrt{X_i^\alpha X_i^\beta}\right) \quad (9)$$

Substitution of this equation into Equation 8 gives the final interfacial equation of state as,

$$\exp\left(-\frac{a}{RT}\sigma\right) - \exp\left(-\frac{a}{RT}\sigma_0\right) = \left(X_s^\alpha \gamma_{s\pm}^\alpha\right) \quad (10)$$

or in more simplified form as,

$$\sigma_0 - \sigma = \pi = \frac{RT}{a} \ln \left[1 + \left(X_s^\alpha \gamma_{s\pm}^\alpha\right) \exp\left(\frac{a}{RT}\sigma_0\right) \right] \quad (11)$$

where σ_0 is the interfacial tension before addition of surfactant. The above equation is similar to the Szyskowski equation but with defined rather than empirical parameters. Equation 11 can be used for prediction of oil/water interfacial tension in presence of an ionic surfactant, provided that the activity coefficient of the surfactant is known at the bulk liquid phase. There have been few reports on the activity coefficient of surfactants in aqueous solutions (see references^{16, 17}). However, since the surfactant solutions are mainly studied in the dilute region, these models provide the activity coefficient in the sense of Henry's law. On the other hand, the activity coefficients presented in the above equations are defined with reference to an ideal solution in the sense of the Raoult's law. They are related to each other by Henry's law constant and the vapour pressure of the surfactant. Many surfactant molecules in pure conditions are in solid form and a precise measurement of their vapour pressure is very difficult, hence few reported values of measured activity coefficients for surfactant molecules in the aqueous phases.

The surfactant's activity coefficient can be reasonably assumed constant over the entire range of the concentration up to the *cmc*.¹⁵ Since the Raoult activity coefficient in the micelle at the *cmc* ($\gamma_{\pm}^{\text{micelle}}$) is unity, the activity coefficient at the bulk can then be calculated by

$$X_{s+}^{\alpha} X_{s-}^{\alpha} (\gamma_{\pm}^{\alpha})^2 = X_{s+}^{micelle} X_{s-}^{micelle} (\gamma_{\pm}^{micelle})^2 \quad \text{at } X_s = cmc \quad (12)$$

Therefore;

$$\gamma_{\pm}^{\alpha} = \frac{1}{2cmc} \quad (13)$$

It should be noted that the effect of micellar curvature is neglected in the above equations. The micellar curvature results in a pressure difference between the bulk and micelle, known as capillary pressure. This pressure relates to the interfacial tension between the micelle and the bulk liquid phase and also to the molar volume of the micellar core. The interfacial tension between micelles and the bulk liquid phase is almost negligible and hence there is no significant capillary pressure. Substitution of the above equation in Equation 11, for a 1:1 ionic surfactant, results in the following interfacial equation of state:

$$\sigma_0 - \sigma = \pi = \frac{RT}{a} \ln \left[1 + \frac{X_s^{\alpha}}{2cmc} \exp \left(\frac{a}{RT} \sigma_0 \right) \right] \quad (14)$$

Before implementation of this equation we need to know the value of molar surface area, a . It has been recently shown¹⁴ that molar surface area is the characteristic value of a system related to the maximum adsorption amount. For water/hydrocarbon systems it is found that $a = 22.22R$. For systems containing surfactants, the molecular surface area of the surfactant can be a sensible value to use. Using this information, the equation is examined in the next section for the prediction of oil/water interfacial tension of some individual ionic surfactant solutions. The impact of multi-layer formation and dissolved organic and ionic compounds on the interfacial behaviour also is discussed.

Results

Single ionic surfactant

The anionic sodium dodecyl sulphate, SDS, and the cationic alkyl tri-methyl ammonium bromide, C_nTAB, are selected to check the validity of the derived equation. The selected molecules SDS and CTAB are almost insoluble in the hydrocarbon phase. Thus, the mole

fraction of a singly dispersed surfactant in the aqueous phase, X_s^α , is equal to the total concentration below the *cmc* and is equal to *cmc* for concentrations above the *cmc*. Both surfactants are widely investigated at air/water and oil/water interfaces by tensiometry^{6, 7, 18-23} and by neutron reflectivity^{15, 24} techniques.

Figure 1 shows the predicted interfacial tension by Equation 14 between n-decane and water with respect to the SDS concentration at 25°C. The experimental data¹⁸ are also included in the figure. The area per molecule of SDS at the air/water interface is found by the neutron reflectivity (NR) method to be about 42 Å².¹⁵ The red line in Figure 1 shows the predicted interfacial tension data using the above value which is obviously lower than the measured data across the range of surfactant concentrations. The blue line presents the fitted values by $a = 25$ Å² ($a = 18.10R$). Interestingly this value is in excellent agreement with the suggested area per molecule of SDS according to Mulqueen.⁴ Similar results are obtained for the effect of the SDS concentration on the interfacial tension between water and various hydrocarbons like n-hexane, n-octane, and n-heptadecane, as shown in Figures 2-4. The discrepancy between area values will be discussed as stemming from the assumption of a monolayer interface.

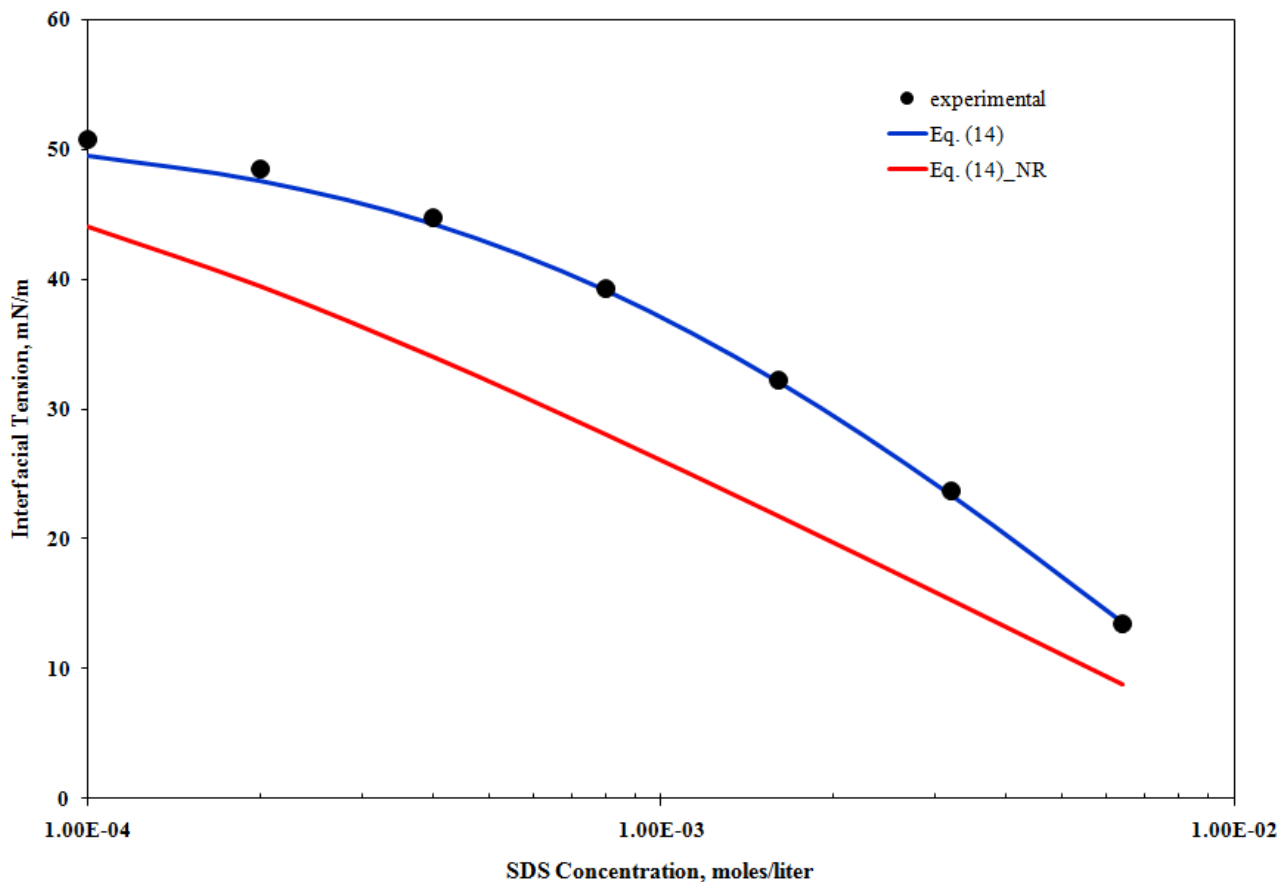


Figure 1. Experimental¹⁸ and predicted interfacial tension of the water/n-decane system as a function of SDS concentration. The blue line is the predicted data with $a = 25 \text{ \AA}^2$ ($a = 18.10R$). The red line shows the predicted values using the measured area per molecule of SDS at air/water surface by neutron reflectivity (NR) technique ($a = 42 \text{ \AA}^2$ or $30.41R$)¹⁵. This discrepancy is resolved by considering the formation of a multilayer interface in Equation 18.

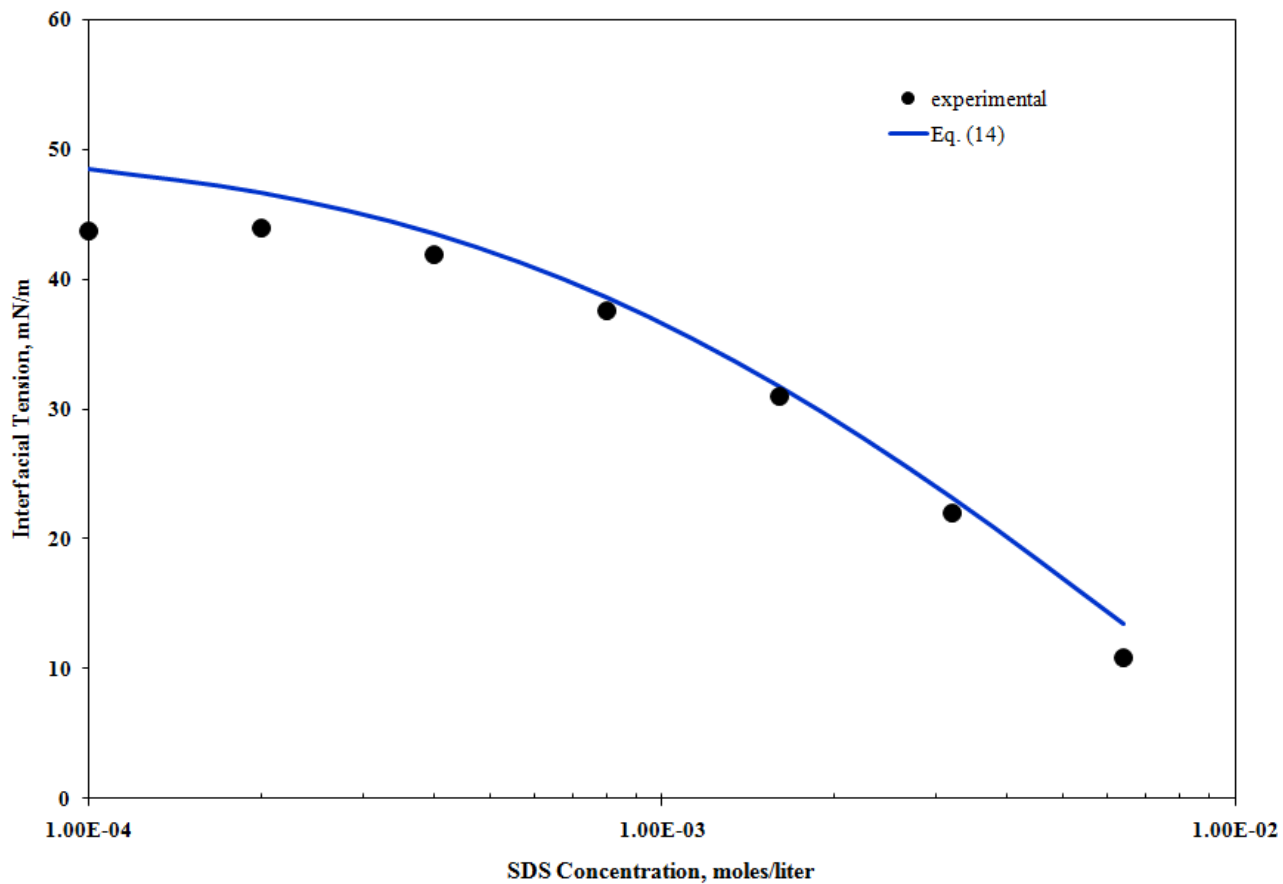


Figure 2. Experimental¹⁸ and predicted interfacial tension (with $a = 25 \text{ \AA}^2$) of the water/n-hexane system as a function of SDS concentration.

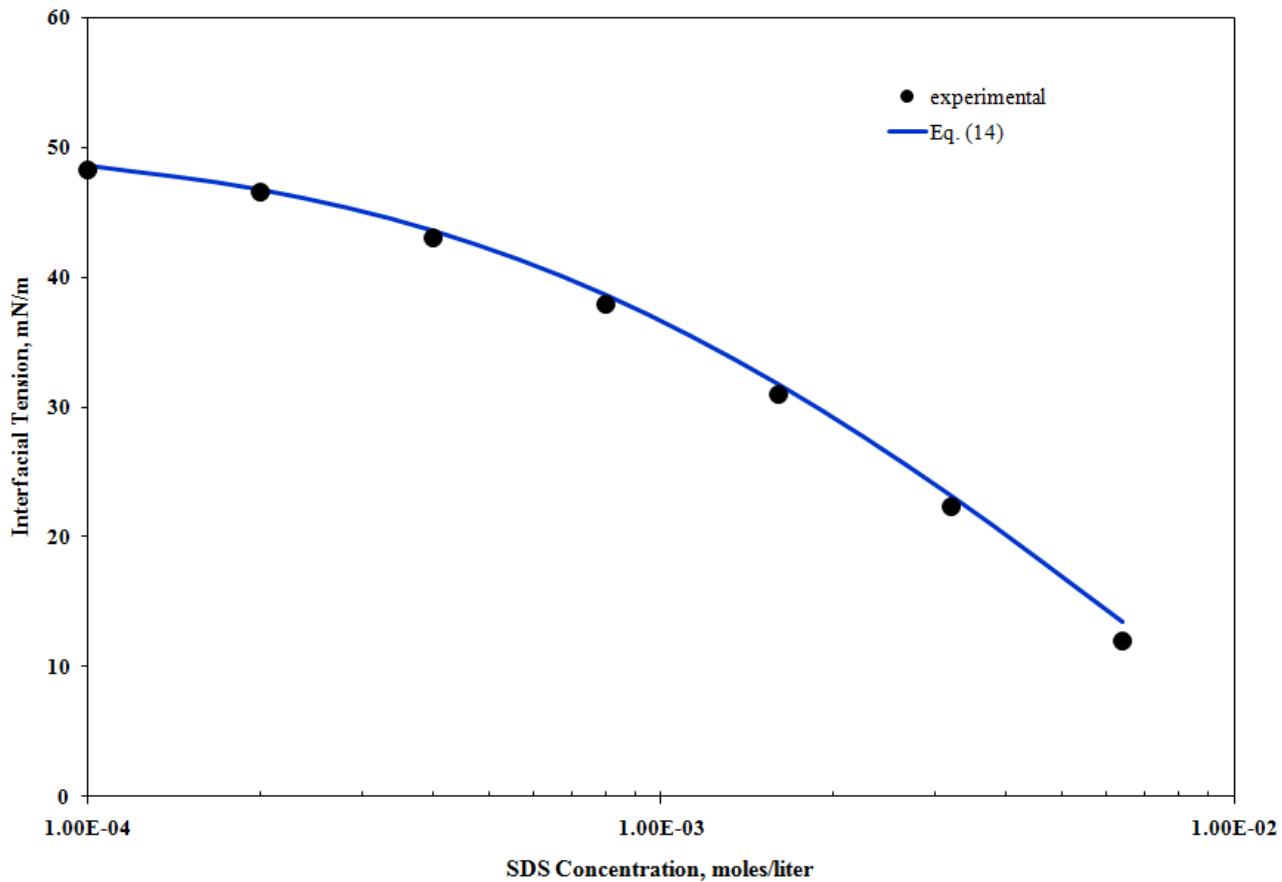


Figure 3. Experimental¹⁸ and predicted interfacial tension (with $a = 25 \text{ \AA}^2$) of the water/n-octane system as a function of SDS concentration.

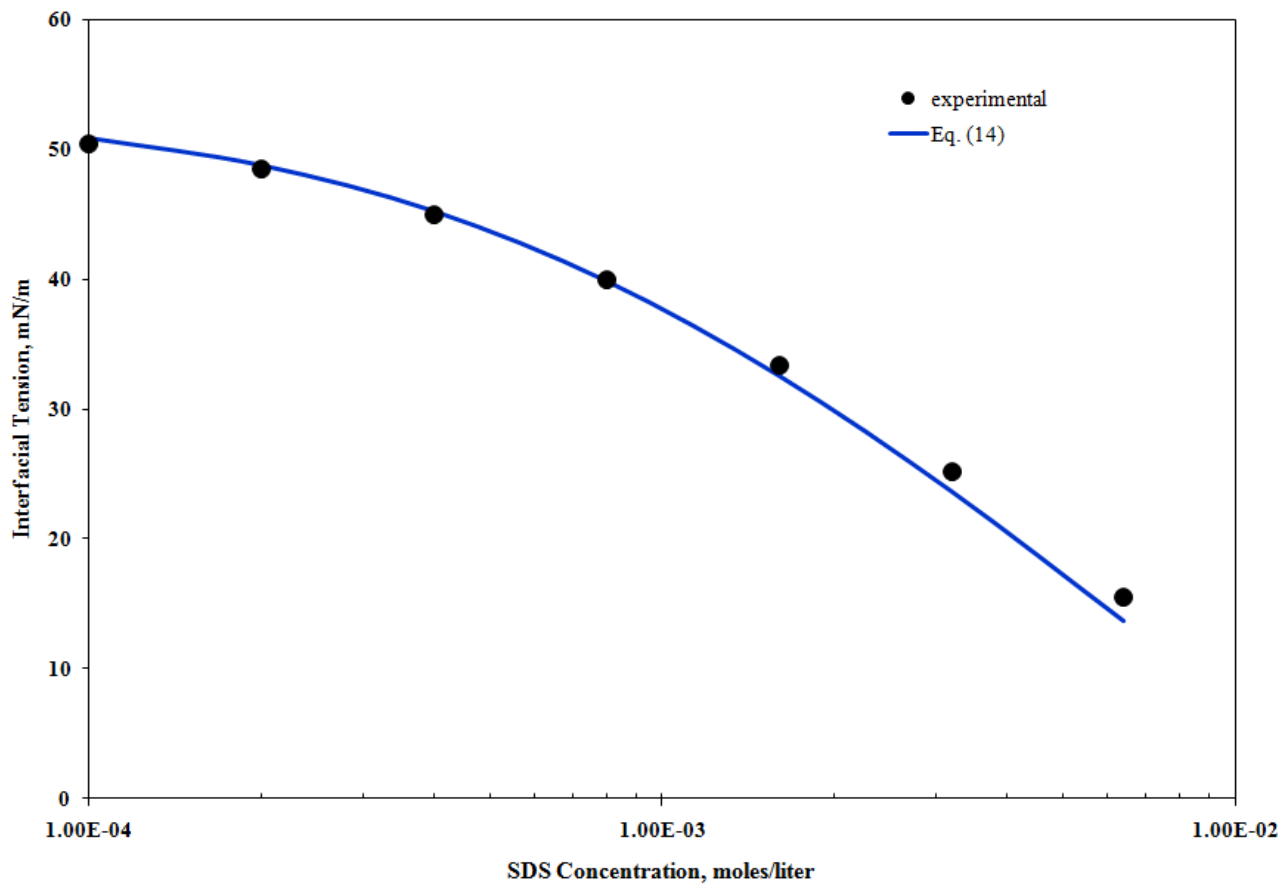


Figure 4. Experimental¹⁸ and predicted interfacial tension (with $a = 25 \text{ \AA}^2$) of the water/n-heptadecane system as a function of SDS concentration.

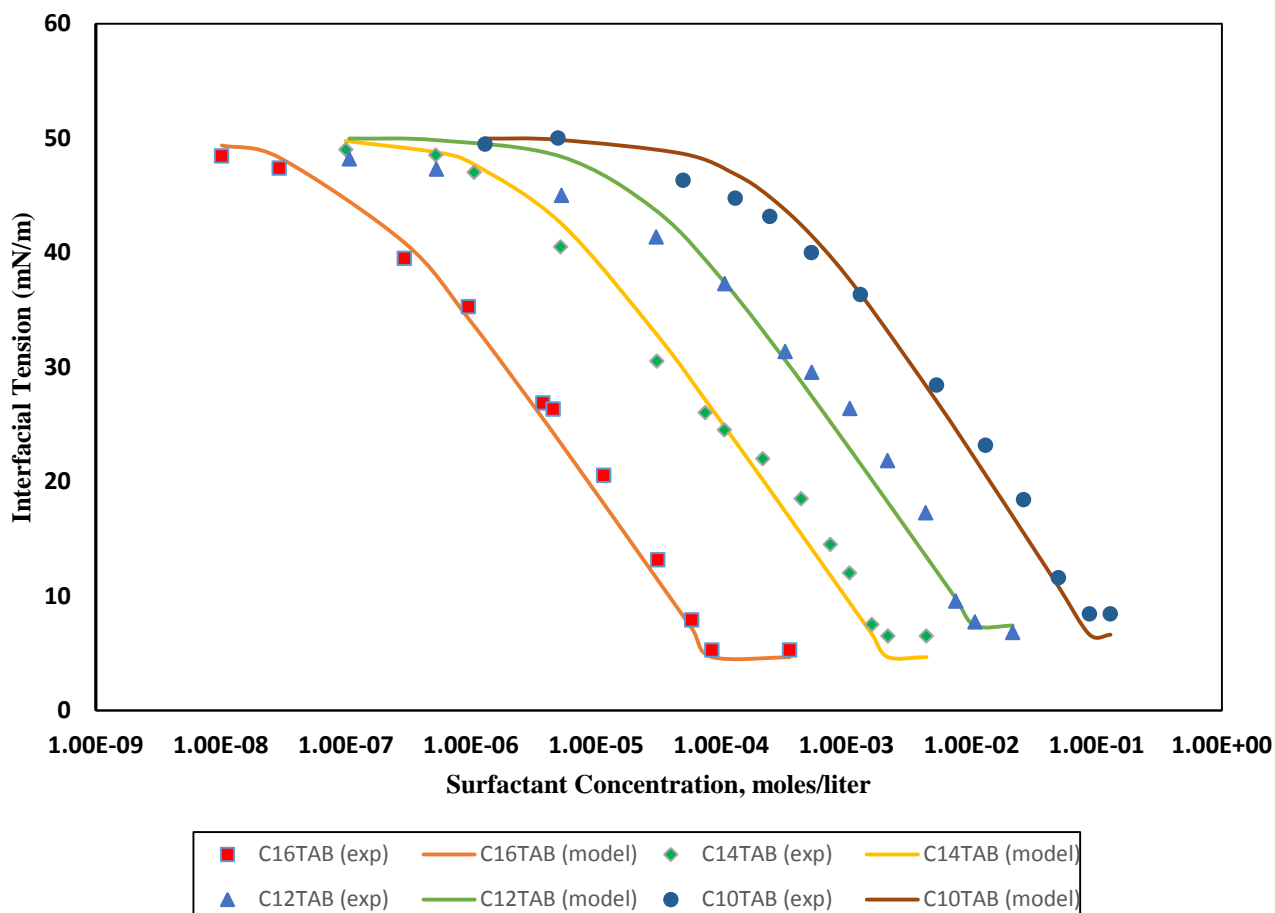


Figure 5. Interfacial isotherms of C_n TAB at the water/n-hexane interface. Experimental data are from Fainerman et. al.⁷ The solid lines are predicted values using Equation 14 (with $a = 61 \text{ \AA}^2$). The fitted a value is half the value obtained by the neutron scattering technique, indicating a multi-layer interface (Equation 18).

Figure 5 depicts the predicted values as well as the experimental data⁷ of interfacial tensions between n-hexane and water with respect to the concentration of C_n TAB. All the predicted values are obtained using $a = 61 \text{ \AA}^2/\text{molecule}$. This value is far away from the experimental values obtained by NR for C_{14} TAB at the air/water interface ($=45 \text{ \AA}^2$), and also at the n-hexadecane/water interface ($= 124 \text{ \AA}^2$ assuming the surfactant resides in the oil phase and $= 85 \text{ \AA}^2$ assuming surfactant residing in the aqueous environment).²⁴ Zarbakhsh et al., however, explain that the interfacial structure of this system is composed of a bilayer or fragmented bilayer/micellar phase below the primary interfacial layer (a trilayer). Equation 14, however, is

based on assuming the interface as a monolayer. For a multi-layer interface, the interfacial tension is the sum of all tensions in those layers;¹⁴

$$\sigma^{\alpha\beta} = \sum_i \sigma^i \quad (15)$$

where σ^i is the interfacial tension of i th layer. It can be reasonably assumed that middle layers have a zero or negligible interfacial tension, because the layers below and above are closely similar. Mostly, the upper and lower layers, however, experience different environments and hence exhibit nonzero interfacial tensions. The interfacial tension in these layers follows (not rigorously but for the sake of simplicity) a similar equation to Equation 14;

$$\sigma_0^i - \sigma^i = \frac{RT}{a} \ln \left[1 + \frac{X_s^a}{2cmc} \exp \left(\frac{a}{RT} \sigma_0^i \right) \right] \quad (16)$$

When there is no surfactant in the system, the above discussion results in

$$\sigma_0^i = \frac{\sigma_0}{2}; i = 1, n \quad (17)$$

Therefore the interfacial tension for an n -layer interface is

$$\sigma_0 - \sigma = 2 \frac{RT}{a} \ln \left[1 + \frac{X_s^a}{2cmc} \exp \left(\frac{a\sigma_0}{2RT} \right) \right] \quad (18)$$

This equation is similar to 14, replacing “ a ” with “ $a/2$ ”. Using Equation 18 for the case of C₁₄TAB results in $a = 122 \text{ \AA}^2$. This value is in excellent agreement with the area values obtained by NR ($=124 \text{ \AA}^2$).²⁴ Equation 18 also gives $a = 50 \text{ \AA}^2$ per SDS molecule which is exactly that which is calculated from Gibbs isotherm¹⁸, and is closely in line with the measured value by the small-angle neutron scattering technique ($a = 48 \text{ \AA}^2$) at hexadecane-water interface.²⁵

Interfacial Equation of State in the Presence of Salt

When the dissolved salt has a common ion with the surfactant, e.g. Na⁺ in SDS and NaCl, then the molar fraction of counter ion must be modified. Thus, denoting superscript c as common ion, for a 1:1 surfactant,

$$X_{s(\pm)}^{\alpha,c} = X_s^\alpha + X_{salt}^{common} \quad (19)$$

$$X_{s(\pm)}^{\alpha\beta,c} = \beta X_s^{\alpha\beta} \quad (20)$$

The unknown β coefficient modifies the adsorption value of the common ion in presence of dissolved salt. When there is no salt, it is equal to unity. The interfacial tension of the oil/water system is reported to increase almost linearly with salt concentration²⁶ which is due to negative adsorption of ions according to Gibbs' equation. Therefore, a β - value lower than unity might be expected in high electrolyte concentrations. The above modifications change Equation 18 to,

$$\sigma_0 - \sigma = 2 \frac{RT}{a} \ln \left[1 + \frac{\sqrt{X_s^\alpha (X_s^\alpha + X_{salt}^{common})}}{2\beta \sqrt{cmc (cmc + X_{salt}^{common})}} \exp\left(\frac{a\sigma_0}{2RT}\right) \right] \quad (21)$$

The cmc of ionic surfactants decreases normally by the addition of salts.²⁷ Thus, when the dissolved salt has no common ion with the surfactant ($X_{salt}^{common}=0$), its impact on the interfacial tension is just through variation of cmc and its β - factor. Figure 6 shows the interfacial tension of SDS at the water/n-hexadecane interface in the presence of NaCl. Predicted values are obtained by Equation 21, and using $a = 50 \text{ \AA}^2$. The β - value is set to 1 at low salt concentrations and equal to 0.8 at 0.15M NaCl. As discussed above, this lower value is due to the negative adsorption of the counter ion in an electrolyte environment. However, the reasonable fit of the Equation 21 to the experimental values reveals the reliability of the proposed model, proposing also a new method for the investigation of ionic adsorption at the oil/water interface.

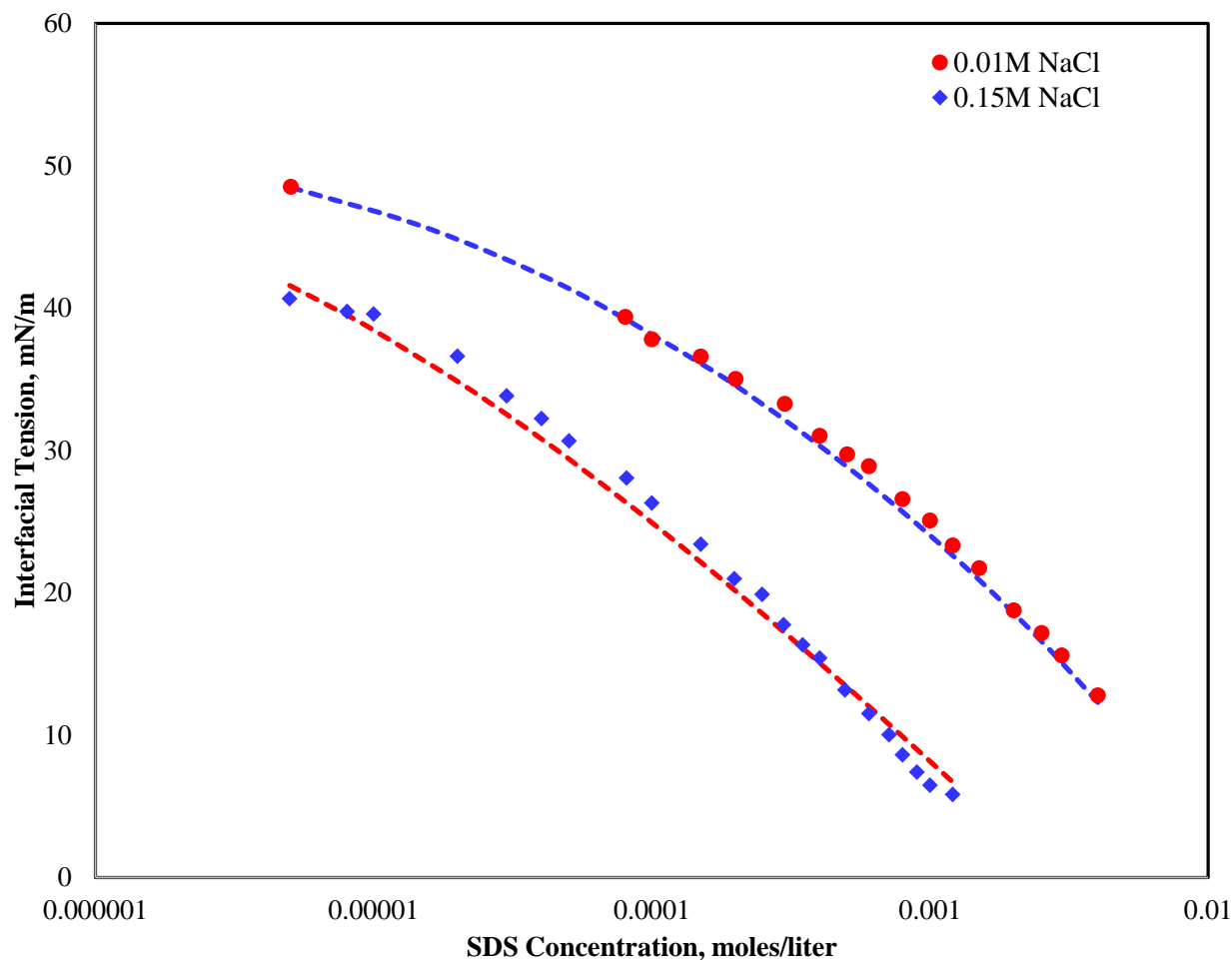


Figure 6. Interfacial isotherms of SDS at the water/n-hexadecane interface in presence of NaCl. Experimental data are from Gurkov et. al.²⁸ The dash lines are predicted values using Equation 21 (with $a = 50 \text{ \AA}^2$). β is set to one for 0.01M NaCl and to 0.8 for 0.15M NaCl. Therefore, there is about 20 percent less adsorption of counter ions in the concentrated electrolyte.

In all the above investigated cases, the solubility of the oil phase in the water phase is negligible. The solubility of the oil into the water phase can considerably affect the surfactant properties. For instance, presence of organic molecules in the water phase can facilitate the formation of micelles. They can work as nuclei and contribute into the micellar phase as spacers. As a result, they lower the electrostatic repulsion between charged head groups and hence they lower the *cmc*. In the next section, the model is developed to consider the effect of oil solubility on the interfacial tension in presence of ionic surfactants.

Effect of dissolved organic liquid

As mentioned in the previous section, the presence of dissolved oil can increase the tendency of surfactant molecules to form micelles, hence lower *cmc*. Moreover, the organic component contributes to the micellar formation and changes the composition at the micellar phase. Additionally, the presence of oil components within the micellar phase deteriorates the ideal behaviour of the micellar phase. Considering the presence of organic molecules in the micelles the activity coefficient of surfactant at the bulk is;

$$\gamma_{s\pm}^{\alpha} = \frac{\lambda}{cmc_{s\pm}} \quad (22)$$

where, λ accounts for the activity of surfactant ions and counter ions in the micellar phase ($= \frac{1}{2} X_s^{micelle} \gamma_s^{micelle}$). Its value for the case of pure micelles is $\frac{1}{2}$, reducing the above equation to the Equation 13 for monovalent surfactants. The mole fraction of the organic molecules in the micellar phase, therefore, would be proportional to $1-2\lambda$ for ideal aggregates. Equation 18 for systems involving with considerable dissolution of the oil component into water, thus, reduces to;

$$\sigma_0 - \sigma = \pi = 2 \frac{RT}{a} \ln \left[1 + \frac{\lambda X_s^{\alpha}}{cmc} \exp \left(\frac{a}{2RT} \sigma_0 \right) \right] \quad (23)$$

In the above equation, the *cmc* is the *cmc* value at oil saturated water phase. Figure 7 shows the variation of experimental¹⁸ water/cyclohexane interfacial tension with respect to the concentration of SDS. The predicted values also are included in this figure, considering different λ values. It is evident that considering the effect of dissolved oil on the micellar properties has notably improved the predicted results. The results show that λ values higher than $\frac{1}{2}$ correspond better with the experimental data. This fact evidently shows the positive deviation of surfactant-oil mixture from the ideal solution behaviour. Therefore, the surfactant has higher activity in presence of dissolved oil and as a consequence shows more adsorption into the interface.

Much higher improvement can be seen for the case of water/benzene (Figure 8). The solubility of benzene in the water phase is much higher than the cyclohexane and also many other

hydrocarbons. The *cmc* value of SDS in hydrocarbon saturated water is found¹⁸ to be the lowest for benzene which is the most unsaturated molecule. The decrease in *cmc* of some other surfactants like dodecyl ammonium chloride^{29, 30}, potassium carboxylate³¹, sodium alkyl sulfonates and potassium dodecyl sulfonates³² in presence of dissolved benzene, toluene, and some other hydrocarbons also is reported by some investigators. The *cmc* values of these surfactants also are reported to be reduced to their lowest values in the presence of benzene. However, according to the Figure 8, the activity of the surfactant at the micellar phase seems to be close to 2/3. If we assume that micelles are equimolarly formed by surfactant and benzene, i.e. $X_s^{micelle} = 0.5$, and furthermore we consider the system as a regular solution, then the above-obtained value for the activity of the surfactant will result in a value of 2.67 for the activity coefficient of benzene at the micellar phase. This result is in reasonable agreement with the reported value of 2.10 by Rehfeld.¹⁸ Rehfeld used also the differential absorption spectroscopy to determine the amounts of benzene dissolved in micellar core and found a mole fraction of 0.47 for benzene, which is in agreement with the above equimolar assumption. These results confirm the reliability of the new developed model. The model can be further developed for systems comprising mixtures of surfactants. However, the ideal or non-ideal state of the mixed surfactant at the interface must be considered as a main challenge.

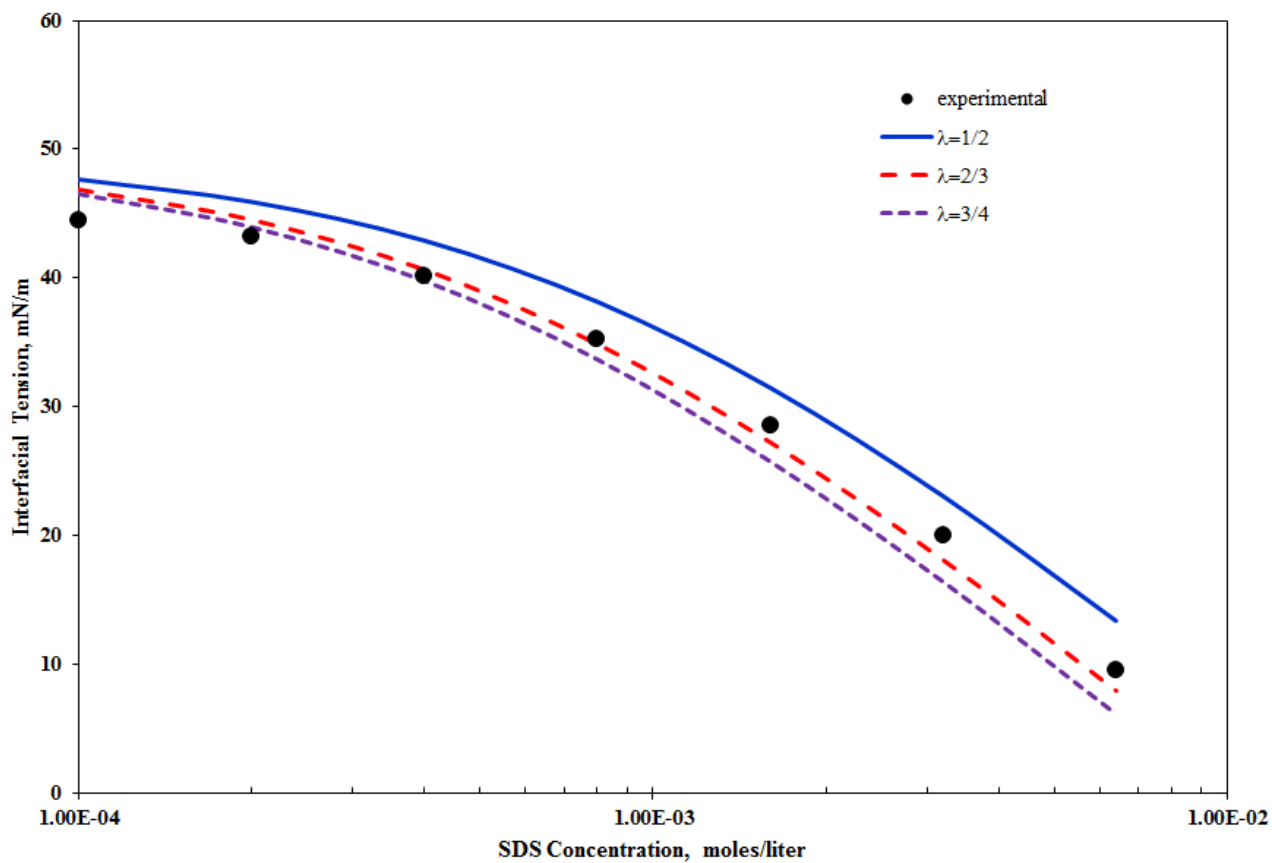


Figure 7. Experimental¹⁸ and predicted interfacial tension of the water/cyclohexane system as a function of SDS concentration in the aqueous phase. The predicted values with different λ values are obtained by Equation 23, accounting for the effect of oil solubility on the interfacial behaviour.

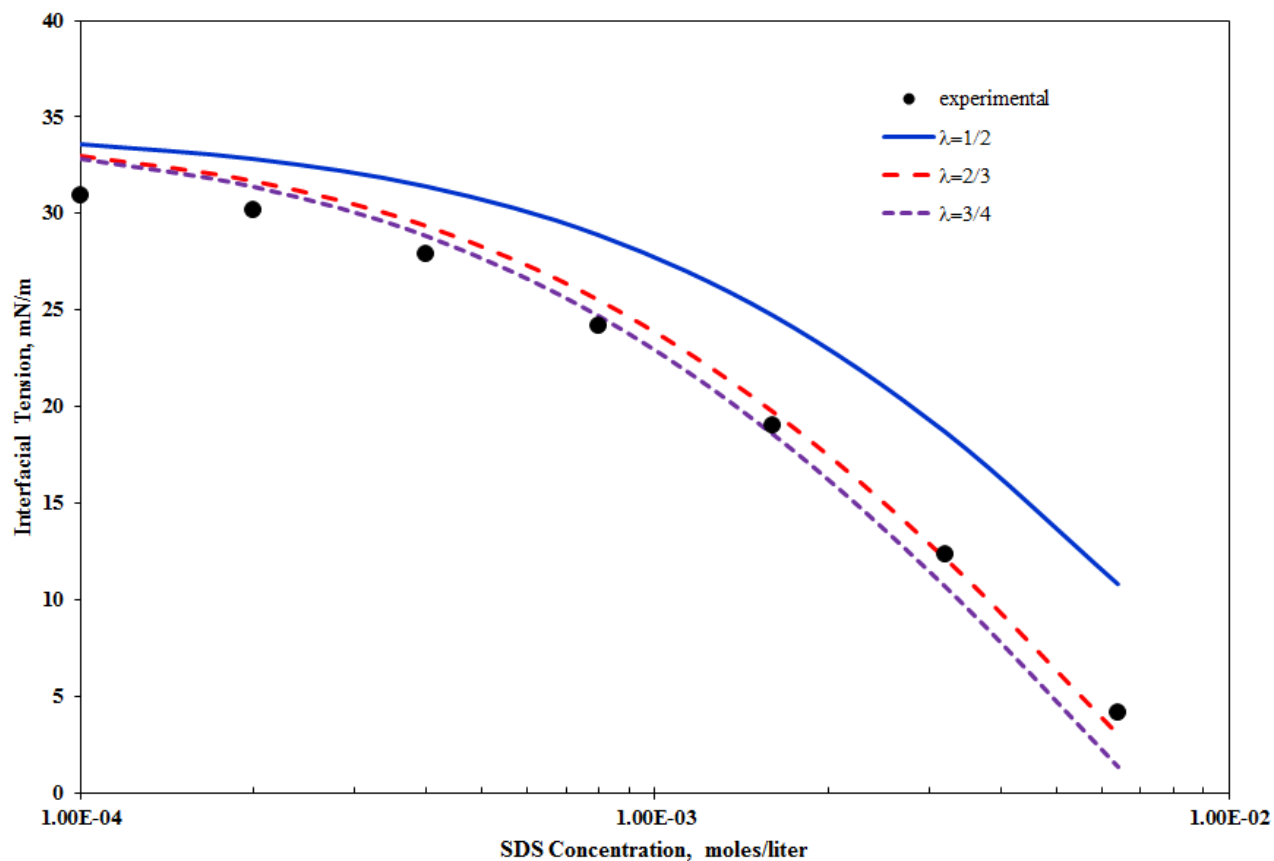


Figure 8. Experimental¹⁸ and predicted interfacial tension of the water/benzene system as a function of SDS concentration in the aqueous phase. The predicted values with different λ values are obtained by Equation 23, accounting for the effect of oil solubility on the interfacial behaviour.

Conclusion

The recently developed model for the interfacial tension of oil/water systems is developed to include ionizing surfactants. Using the work of Lucassen-Reynders⁸ about the formation of ideal surfaces by ionized surfactants at the oil/water interface, a new interfacial equation of state is developed. The new equation can reliably describe the interfacial behaviour of oil/water systems in presence of ionized surfactants. The formation of multi-layer interface is discussed and it is shown that the monolayer assumption, although giving a reasonable fit, results in an area per surfactant molecule far below the measured data by NR techniques. It is shown that the

proposed interfacial equation of state can be simply developed for systems containing electrolytes. The impact of electrolytes is shown to be on the *cmc*, lowering surfactant activity at the bulk phase, and on the counter ion adsorption. The developed model, thus, can employ interfacial tension data to evaluate the ionic desorption or adsorption in electrolyte environment. The discussion has also considered the effect of dissolved oil on the interfacial behaviour of the surfactants in an oil/water system. It is shown that the activity of surfactant molecules at the mixed micelle of oil and surfactant positively deviates from the ideal solution behaviour. This behaviour simply explains the little or no partitioning of the surfactant molecule into the oil phase and also explains the lower interfacial tension in presence of dissolved oil. The new interfacial equation of state can be simply and reliably used for prediction of oil/water interfacial tension in presence of ionized surfactants, provided that the molecular structure of surfactant and the *cmc* value of the surfactant in the aqueous phase is known.

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Interfacial Equation of State for Ionized Surfactants at Oil/Water Interfaces

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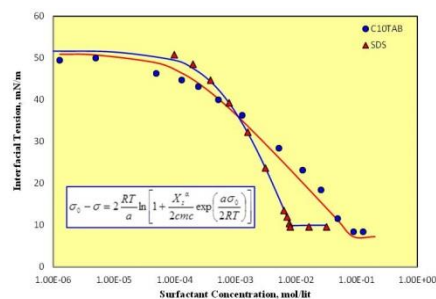
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Predicted and experimental interfacial tension isotherms at the oil-water interface as a function of SDS and C10TAB concentration.

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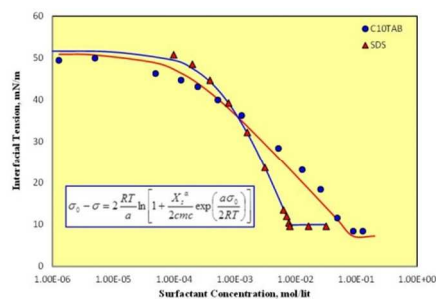
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