Thermodynamic Investigation of Cationic Surfactants Effect on Oil-Water Interfacial Tension

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ABSTRACT: Multi-phase fluid flow through porous media is strongly dependent on interfacial tension of immiscible fluids. Fluid mechanics will be affected by changing the interfacial tension. This paper describes a new approach to predict the interfacial tension at the oil-water system in the presence of an ionic surfactant. This study equation is based on Butler equation, often used for obtaining surface tension equations at different interfaces. The Debye–Hückel theory is used to determine activity coefficients of surfactant in the bulk phase. Cationic surfactants, including decyl trimethylammonium bromide ($C_{10}TAB$) and dodecyl trimethylammonium bromide ($C_{12}TAB$), are used to validate the equation. The new final equation can properly describe the alkane-water interfacial tension in the presence of single surfactant solutions. In this study, alkanes, including hexane, heptane, octane, decane, dodecane, and tetradecane are considered as the oil phase. The following parameters are obtained by curve-fitting: 1- molar surface area, and 2- bulk-surface distribution coefficient of surfactant. The alteration of equation parameters at different alkane-water systems is discussed. The newly developed equation is in a good agreement with the literature experimental data. This approach can be particularly important in the practical use of surfactants for the reduction of oil-water interfacial tension when experimental data are rare.

1- Introduction

A surface active agent (surfactant) when presented at low concentration in a system can adsorb onto the interfaces (surface) of the system and of altering to a noticeable degree the interfacial free energies of those interfaces. The term "interface" shows a boundary between any two immiscible phases; the term "surface" indicates an interface where one phase is a gas [1].

Some human action deals with surfactants. A growth evolution for surfactants in the petroleum industry began during the sixties. Methods of injecting water and gas into the reservoir (secondary oil recovery) began to be widely used to control the pressure drop as a feature of oil reservoir structure. These methods left 50 to 70% of the original oil in a place. Thus, experiments and the applied trials were begun on the progress of enhanced oil recovery techniques [2].

A theory capable of predicting the interfacial tensions of aqueous solutions containing surfactants would alleviate the need for time consuming experimental investigation. The effect of surfactants on the interfacial tension is often described by a surface equation of the state. To obtain surface equations of the state, different approaches are reviewed by Lucassen-Reynders [3].

This study presents a new interfacial equation of the state for ionized surfactants at oil–water interfaces. This equation is simple and requires only two fitting parameters. As it will be seen, the new equation can be satisfactorily used for the prediction of alkane-water interfacial tension in the presence of a single ionic surfactant.

2- Theory

The Butler equation often used for the derivation of surface equations of the state and adsorption isotherms, is as follows:

$$\mu_i^{\alpha\beta} = \mu_i^{0,\alpha\beta} + RT \ln f_i^{\alpha\beta} x_i^{\alpha\beta} - \sigma\omega_i \qquad (1)$$

where chemical potentials $\mu_i^{\alpha\beta}$ depend on the composition of the layer and their surface tension σ; the superscript $\alpha\beta$ refers to the surface (interface), $\mu_i^{0,\alpha\beta}$ is the standard chemical potential, R is universal gas constant, T is the temperature, f_i is the activity coefficient, x_i is the mole fraction, and ω_i is the partial molar area of the ith component.

For the chemical potentials of the components in the solution bulk we have:

$$\mu_i^{\alpha} = \mu_i^{0,\alpha} + RT \ln f_i^{\alpha} x_i^{\alpha} \qquad (2)$$

where the superscript α refers to the bulk solution.

Eqs. (1) and (2) for 1:1 ionic surfactant ZY, and with the definition of mean ionic mole fractions, $x_{\pm}$, and mean ionic activity coefficient, $f_{\pm}$ take the form

$$\mu_{ZY}^{\alpha\beta} = \mu_{ZY}^{0,\alpha\beta} + 2RT \ln f_{ZY\pm}^{\alpha\beta} x_{ZY\pm}^{\alpha\beta} - \sigma\omega_{ZY} \qquad (3)$$

$$\mu_{ZY}^{\alpha} = \mu_{ZY}^{0,\alpha} + 2RT \ln f_{ZY\pm}^{\alpha} x_{ZY\pm}^{\alpha} \qquad (4)$$

For simplicity, the subscript $\pm$ will be omitted. At equilibrium, from Eqs. (3) and (4) one obtains:

$$\mu_{ZY}^{0,\alpha} + 2RT \ln f_{ZY}^{\alpha} x_{ZY}^{\alpha} = \mu_{ZY}^{0,\alpha\beta}$$
$$+ 2RT \ln f_{ZY}^{\alpha\beta} x_{ZY}^{\alpha\beta} - \sigma\omega_{ZY} \qquad (5)$$

The bulk-surface distribution coefficient of ith component K_i,

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and bulk-surface distribution coefficient of surfactants K_{ZY} are defined by

$$K_i = \exp\left(\frac{\mu_i^{0,\alpha\beta} - \mu_i^{0,\alpha}}{2RT}\right) \qquad (6)$$

$$K_{ZY} = \exp\left(\frac{\mu_{ZY}^{0,\alpha\beta} - \mu_{ZY}^{0,\alpha}}{2RT}\right) \qquad (7)$$

Inserting Eq. (7) into Eq. (5) gives

$$\frac{\sigma\omega_{ZY}}{2RT} = \ln\left(\frac{K_{ZY} f_{ZY}^{\alpha\beta} x_{ZY}^{\alpha\beta}}{f_{ZY}^{\alpha} x_{ZY}^{\alpha}}\right) \qquad (8)$$

For ideal interfaces, $f_i^{\alpha\beta}=1$. Summation of mole fractions at the interface must equal unity. Thus

$$\frac{f_{ZY}^{\alpha} x_{ZY}^{\alpha}}{K_{ZY}}\exp\left(\frac{\sigma\omega_{ZY}}{2RT}\right) + \sum\frac{f_i^{\alpha} x_i^{\alpha}}{K_i}\exp\left(\frac{\sigma\omega_i}{2RT}\right) = 1 \qquad (9)$$

With an approximation ($\omega_i = \omega$)

$$\exp\left(\frac{\sigma\omega}{2RT}\right)\left[\frac{f_{ZY}^{\alpha} x_{ZY}^{\alpha}}{K_{ZY}} + \sum\frac{f_i^{\alpha} x_i^{\alpha}}{K_i}\right] = 1 \qquad (10)$$

When there is no surfactant in the system

$$\exp\left(\frac{-\sigma_0\omega}{2RT}\right) = \sum\frac{f_i^{\alpha} x_i^{\alpha}}{K_i} \qquad (11)$$

where σ_0 is the interfacial tension of the system without surfactant. Inserting Eq. (11) into Eq. (10) gives

$$\exp\left(\frac{-\sigma\omega}{2RT}\right) - \exp\left(\frac{-\sigma_0\omega}{2RT}\right) = \frac{f_{ZY}^{\alpha} x_{ZY}^{\alpha}}{K_{ZY}} \qquad (12)$$

Eq. (12) can be written in a more efficient form

$$\pi = \sigma_0 - \sigma = 2\frac{RT}{\omega}\ln\left[1 + \frac{f_{ZY}^{\alpha} x_{ZY}^{\alpha}}{K_{ZY}}\exp\left(\frac{\omega\sigma_0}{2RT}\right)\right] \qquad (13)$$

An equation accurately representing measured values of the average activity coefficient f_{ZY}^{α} is the Debye–Hückel theory.

3- Results and Discussion

The best-fit model parameters obtained from Eq. (13) for alkane-water interfaces are listed in Table 1.
Fig. 1 shows the predicted interfacial tension by this study equation at the dodecane-water interface as a function of C_{10}TAB and C_{12}TAB concentration at 25°C.
Fig. 2 compares the Average Absolute percentage Deviation (AAD%) values of Eq. (13) for C_{10}TAB and C_{12}TAB solutions at the alkane-water interfaces.

4- Conclusions

A new equation to predict interfacial tension at oil-water interfaces in the presence of ionic surfactants is developed based on Butler equation. By fitting literature data with the equation, molar surface area ω and bulk-surface distribution coefficients of surfactants K_S are obtained. At alkane-water interfaces in the presence of C_{10}TAB and C_{12}TAB for each

Table 1. Best-fit parameters of Eq. (13) for C_{10}TAB and C_{12}TAB solutions at the alkane-water interfaces; experimental data are taken from the literature [4]

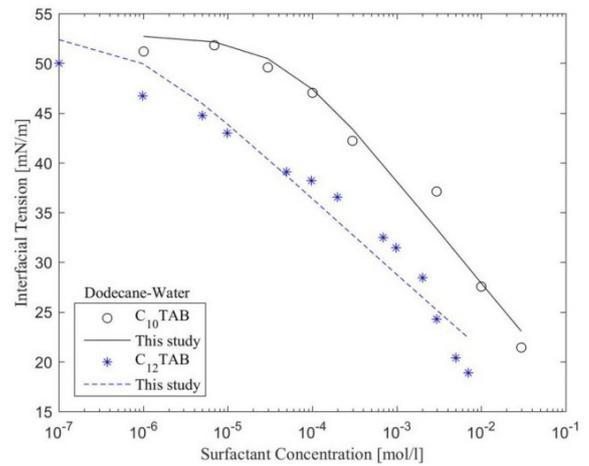| Type of interface vs. water-C$_n$TAB	ω [Å²]		K_s	
	n=10	n=12	n=10	n=12
Hexane	133.8	135	51e-4	8.6e-4
Heptane	116.2	163.5	86e-4	30e-4
Octane	118	143	100e-4	9.4e-4
Decane	119	178	77e-4	27e-4
Dodecane	176	247	63e-3	95e-3
Tetradecane	66.1	168	26e-4	62e-4

Figure 1. Interfacial tension isotherms of C_{10}TAB and C_{12}TAB at the dodecane-water interface; lines correspond to the curves calculated by the Eq. (13) at 25°C; experimental data are taken from the literature [4]
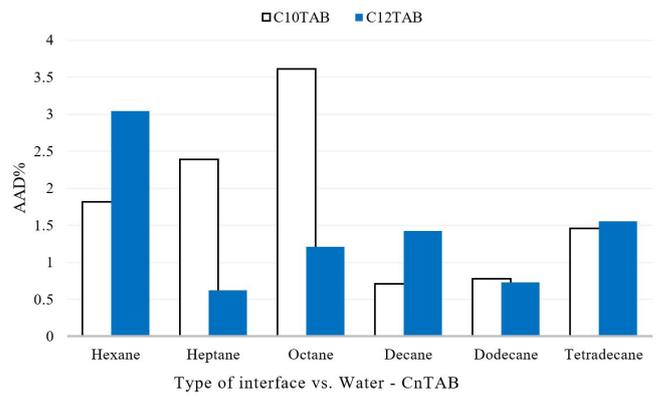

Figure 2. Comparison of the AAD% values at the alkane-water interfaces in the presence of C_{10}TAB and C_{12}TAB

of the alkanes, ω values are increased by increasing the surfactant's molecular weight. The agreement of the new equation with experimental data was reasonable in the concentration region below and near the Critical Micelle Concentration (CMC).

References

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