Adsorption and Interfacial Properties of Individual and Mixtures of Cationic/Nonionic Surfactants in Toluene + Water Chemical Systems

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The influence of individual and binary adsorption of octylphenol decaethylene glycol ether (Triton X-100) and dodecyl trimethyl ammonium chloride (DTMAC) surfactants with bulk compositions within $(1.50 \cdot 10^{-6}$ to $4.80 \cdot 10^{-4})$ $\text{mol} \cdot \text{L}^{-1}$ on the interfacial tension of a recommended system for liquid−liquid extraction investigations, toluene + water, at 25.0 °C is studied. The drop-weight method has been used to measure the interfacial tension, and a maximum relative standard deviation of ± 0.01 has been appropriate for the concentration of surfactant solutions. From the data and in agreement with the commonly used Szyszkowski equation, a much higher adsorption effectiveness and adsorption tendency for Triton in comparison with DTMAC is obtained. The influence of DTMAC in lowering interfacial tension can be enhanced significantly by adding Triton with bulk mole fraction less than 0.01. For bulk mole fractions up to about 0.2, the estimated interfacial composition and attractive interaction from the theory of nonideal interactions in binary mixtures show different trends. Accordingly, the attractive interaction parameter finds a maximum absolute value at the bulk mole fraction of about 0.01 and lower values at bulk mole fractions between 0.05 and 0.1. Moreover, investigations on the experimental and ideal area per molecule at the interface show variations in agreement with the interaction parameter.

Introduction

Interfacial tension is one of the physical properties that must be known for the design and operation of two fluid contactors since it affects the hydrodynamics and contact of phases for mass transfer purposes. Interfacial tension is defined as the work to create a unit of new surface between two immiscible fluids.[1] This property plays an important role for instance in improved oil recovery[2] and in sweetening of liquefied petroleum gas (LPG) by aqueous solvents.[3]

Surfactants are widely used in industry for hydrodynamic performance improvement and as foam and emulsion stabilizers.[4] In this regard and for many cases, addition of the individual surfactants is not sufficient to reduce the interfacial tension to a value guaranteeing its usefulness in a given process, and this property must be reached to a desired level by addition of different surfactants.[5,6] Surfactant systems used for practical applications usually consist of a mixture of surfactants, since the interfacial tension and other interfacial properties are often different from those of the individual surfactants. For the evaluation of mass transfer performance of a contactor, the knowledge of interfacial tension variation is required to have the hydrodynamic behavior of phases.

In a number of so far recommended chemical systems for liquid−liquid extraction investigations, water has been introduced as the continuous phase.[7,8] Meanwhile, contaminants are usually present to an unknown extent in water and industrial materials. They accumulate at the interface between phases, inhibit circulation within the drops, cause adsorptive barriers to mass transfer across the interface, and change the pattern of drop behavior in the extraction process. In this regard and to study the different roles of contaminants, surfactants are added artificially as simulating industrial contaminants.

In our recent work,[9] the influence of interfacial adsorption of low amounts of surfactant Triton X-100 and hydroxyl ion (appropriate to the practical aqueous phase pH range of 6.00 to 9.37) on the interfacial tension of two chemical systems of toluene + water and cumene + water has been investigated. The aim of this work is to obtain the interfacial tension and properties of the toluene + water system, a recommended and widely used chemical system for liquid−liquid extraction studies,[8] when two commonly used surfactants, Triton X-100 and DTMAC, as nonionic and cationic surfactants are present. Triton X-100 is compatible with anionic, cationic, and other nonionic surfactants, and it possesses wide practical applications in almost every type of liquid, paste, and powdered cleaning compound, ranging from heavy-duty industrial and agrochemical products to gentle detergents.[6] DTMAC is also one of the quaternary ammonium salts that are used as emulsifying agents for acidic emulsions or where adsorption of emulsifying agents onto substrates is desirable.[6] To our knowledge, no study has examined the interfacial adsorption of these surfactant mixtures. The appropriate interfacial composition and the level of interaction between adsorbed species which seem to be very important in studies of the mass transfer are seeked.

Materials and Methods

Materials. The chemical system of toluene + water was used since it has been recommended for experimental investigations in different aspects of the liquid−liquid extraction process.[8] It is used as a high interfacial tension system. Toluene was a Merck product with a purity of more than 99.9 %. The surfactants decaethylene glycol ether octylphenol, $C_{14}H_{22}O(C_2H_4O)_n$ ($n = 9$ to 10, average ≈9.5) (Triton X-100), and dodecyl trimethyl ammonium chloride (DTMAC) were Merck products with purity of more than 99.5 % and 98 %, respectively. These are the most commonly used nonionic and cationic surfactants

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10.1021/je100322t

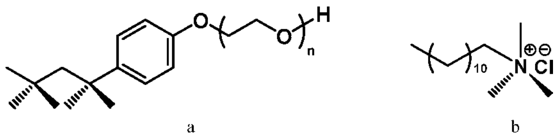

Figure 1. Chemical structure of Triton X-100 (a) and DTMAC (b).

to investigate the role of contaminants in the liquid–liquid extraction process.[10,11] Both the surfactants are water-soluble and were used without further purification. Laboratory distilled water was redistilled prior to experiments. Figure 1 displays the chemical structure of the used surfactants.

Aqueous surfactant solutions were prepared by mass, using a METTLER AE-100 balance with an uncertainty of ± 0.1 mg, 1000 (± 0.6) mL volumetric flasks, and (20 and 25) (± 0.05) mL volumetric pipettes. The relative standard deviation of concentrations (in molarities) has a maximum value of ± 0.01. Surfactant concentrations within ($1.50 \cdot 10^{-6}$ to $4.80 \cdot 10^{-4}$) $\text{mol} \cdot \text{L}^{-1}$ (in total volume samples) were prepared and examined.

To prepare a solution with a specified mole fraction of Triton ($\alpha = c_1/c_{12}$, where c_1 and c_{12} are, respectively, the total bulk molar concentration of Triton and mixture of Triton/DTMAC in both phases), (100.0 or 200.0) mL (depending on α value) of a Triton solution was selected to which the required volume of DTMAC was added. This recent volume was calculated to have the desired α value, with respect to the total solution volume. Volumetric pipettes were used in this regard. At least six different total bulk concentration solutions were prepared for each α value and were used in measurements.

a. Interfacial Tension Measurements. The drop-weight method that has been used in other investigations[10,12−15] was used to determine the interfacial tension of the samples. The drop-forming device and the procedure were similar to that described by our previous works.[12,13] A glass capillary (outer diameter of 4.69 mm) with finely ground tip to give an angle of 90° between the ground face and the internal bore at the end with the edges sharp was used. This thickness was very small, and the formation of a neck between the drop and the capillary tip was not observed under the conditions used in this study; otherwise, this phenomenon should be accounted for to obtain accurate values of interfacial tension.[16] The aqueous phase was held in a narrow glass syringe, conducted by an adjustable syringe pump (Phoenix M-CP, French) and flowed through a rigid tube to the capillary in the stagnant toluene phase. A very low flow rate (1.0 mL in 24.17 min, determined from the flow rate indication when calibrated by measuring the time of syringe piston movement) of the aqueous phase was conducted to the capillary, and drops were formed very slowly at the tip of the capillary.

Each drop volume was obtained from at least six measurements of time. The continuous organic media and conducting tube were thermostatted with an uncertainty of ± 0.1 °C, using an adjustable safety and calibrated thermostat (OPTIMA 740, Japan).

The interfacial tension measurements were carried out at 25.0 °C. Equal volumes (125.0 mL) of both phases (toluene and water) with corresponding aqueous phase concentrations of surfactants were first chosen. To achieve the equilibrium conditions prior to experiments, the samples of both phases in contact with each other were mixed during a period of at least 1 h at 25.0 °C and then remained at rest for 1 h. It is notable that the mutual solubility of organic and aqueous phases is very low and that the formation of emulsion of either phase in another was not observed.

Samples of the organic and the aqueous phases were withdrawn to measure the density. The density of phases was measured by means of an Anton Paar DMA 4500 oscillating U-tube densiometer, provided with automatic viscosity correction. The uncertainty for density measurements was ± 0.01 $\text{kg} \cdot \text{m}^{-3}$. The apparatus was calibrated once a day with dry air and bidistilled fresh water. The desired temperature (25.0 °C) was self-adjusted in this density meter with an uncertainty of ± 0.01 °C.

New main Triton and DTMAC solutions were prepared for each set of three or four experimental points appropriate to individual or to the mixture of surfactants with a specified α value.

b. Calculation of Interfacial Tension. The interfacial tension relationship with the volume of drop (v), falling off the capillary into another phase, is given by Harkins and Brown[17]

$$\gamma = \frac{v \Delta \rho g}{2\pi r f\left(\frac{r}{\sqrt[3]{v}}\right)} \tag{1}$$

where $\Delta\rho$ is the density difference between the aqueous and organic phases (ρ_w and ρ_o); v is the capillary radius; and $f(r/v^{1/3})$ is a constant (dimensionless) which should be obtained from the tables of Harkins and Brown and is correlated in an empirical equation,[18] valid for the range: $0.3 \le r/v^{1/3} \le 1.2$

$$f\left(\frac{r}{\sqrt[3]{v}}\right) = \frac{1}{2\pi}\left[0.167 + 0.193\left(\frac{r}{\sqrt[3]{v}}\right) - 0.0489\left(\frac{r}{\sqrt[3]{v}}\right)^2 - 0.0496\left(\frac{r}{\sqrt[3]{v}}\right)^3\right]^{-1} \tag{2}$$

Recently, Lee et al.[19] have proposed a seven-order polynomial fit equation to experimental data, to extend the range of the variable to $0.0 < r/v^{1/3} < 1.2$

$$f\left(\frac{r}{\sqrt[3]{v}}\right) = 1.000 - 0.9121\left(\frac{r}{\sqrt[3]{v}}\right) - 2.109\left(\frac{r}{\sqrt[3]{v}}\right)^2 + 13.380\left(\frac{r}{\sqrt[3]{v}}\right)^3 - 27.290\left(\frac{r}{\sqrt[3]{v}}\right)^4 + 27.530\left(\frac{r}{\sqrt[3]{v}}\right)^5 - 13.580\left(\frac{r}{\sqrt[3]{v}}\right)^6 + 2.593\left(\frac{r}{\sqrt[3]{v}}\right)^7 \tag{3}$$

The range of $r/v^{1/3}$ (dimensionless) in this work has been within 0.36 to 0.46. The uncertainty in measurement results is estimated to be within ± 0.2 $\text{mN} \cdot \text{m}^{-1}$.

To examine the performance and reliability of the method, the interfacial tension of pure chemical system of toluene and water (binary saturated, without surfactant) at 25.0 °C was compared with reported values in the literature. The obtained value of 36.8 $\text{mN} \cdot \text{m}^{-1}$ is quite close to the reported value of (36.1[2] and 36.6[20]) $\text{mN} \cdot \text{m}^{-1}$.

Results and Discussion

a. General. A range of concentrations, within ($1.50 \cdot 10^{-6}$ to $6.00 \cdot 10^{-5}$) $\text{mol} \cdot \text{L}^{-1}$ of Triton and ($4.50 \cdot 10^{-6}$ to $4.80 \cdot 10^{-4}$) $\text{mol} \cdot \text{L}^{-1}$ of DTMAC, was applied. The used concentrations are far from their critical micelle concentration (CMC) in aqueous

Table 1. Bulk Mole Fraction of Triton, α, Total Concentration of Surfactants, c_t, and Interfacial Tension, γ, Values (at 25.0 °C)

α	$10^6 \cdot c_i$ / $\mathrm{mol \cdot L^{-1}}$	γ / $\mathrm{mN \cdot m^{-1}}$	α	$10^6 \cdot c_i$ / $\mathrm{mol \cdot L^{-1}}$	γ / $\mathrm{mN \cdot m^{-1}}$
0	4.50	35.7	0.2	4.80	32.1
	15.00	34.1		9.60	30.0
	30.00	32.7		24.00	27.4
	45.00	31.7		48.00	25.0
	65.00	30.7		60.00	24.0
	150.00	27.8		240.00	19.3
	300.00	25.5	0.4	4.32	31.4
	480.00	24.1		8.64	29.1
0.005	3.60	35.8		21.60	26.8
	14.40	33.6		43.20	24.6
	36.00	31.0		60.00	23.2
	90.00	28.4		216.00	18.7
	180.00	26.0	0.6	3.96	30.3
	360.00	23.6		7.92	28.4
0.01	3.60	35.6		19.80	25.5
	14.40	32.8		39.60	23.2
	36.00	30.1		59.40	22.1
	90.00	27.5		198.00	18.2
	180.00	25.0	0.8	3.60	29.9
	360.00	22.1		7.20	28.0
0.05	3.60	34.4		18.00	25.4
	14.40	31.6		36.00	22.6
	36.00	29.1		63.00	21.0
	90.00	26.4		180.00	18.3
	180.00	23.8	1	1.50	31.4
	360.00	21.1		3.00	29.2
0.1	3.60	34.2		4.50	28.2
	14.40	30.6		6.00	27.4
	36.00	27.5		15.00	25.3
	90.00	24.9		30.00	22.9
	180.00	22.6		45.00	21.9
	360.00	20.0		60.00	20.9

solutions which are at least $2.2 \cdot 10^{-4}$ mol·L^{-1} for Triton[21,22] and $1.6 \cdot 10^{-2}$ mol·L^{-1} for DTMAC.[23] This low surfactant concentration can be considered as a low level of contamination in an actual liquid−liquid extraction system. Samples containing individual and a mixture of the compounds were investigated. Triton bulk mole fractions of 0.005, 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, and 0.8 were examined for the mixtures of surfactants. The interfacial tension data measured for the toluene + water system at various bulk mole fraction and total bulk surfactant concentrations are listed in Table 1. Due to dilute solutions, the aqueous phase and organic phase densities vary very little within (997.07 to 997.09) kg·m^{-3} and (862.17 to 862.19) kg·m^{-3}, respectively. The interfacial tension values are in the range (18.3 to 35.8) mN·m^{-1} in the presence of surfactants. Drop volumes of within (138.2 to 278.9) mm^3, corresponding to drop formation times of (194.4 to 404.4) s, were generated.

To ensure the achievement of equilibrium conditions in experiments, the variation with drop formation time, obtained with different aqueous phase flow rates, within (0.028 to 0.940) mL·min^{-1}, was investigated. Figure 2 shows the results for Triton, DTMAC, and when the value of α equals 0.1, for instance. Each series of data are with the highest appropriate used surfactant concentration to reflect the influence of adsorption. When the drops are formed rapidly, the surfactant does not have sufficient time to be adsorbed at the interface. The interfacial tension is therefore reflecting an unsteady-state interface. As the time increases, the surfactant continues to accumulate at the interface. Finally, when the time of drop formation becomes very long, depending on the adsorption kinetics of surfactant (more than about 100 s in this work), the interface expansion occurs slowly enough to find equilibrium adsorption and finds no significant change with further drop formation times. This phenomenon in drop weight method has already been reported in the literature.[24,25] The last point of curves in Figure 2 corresponds to the measured values reported in this work.

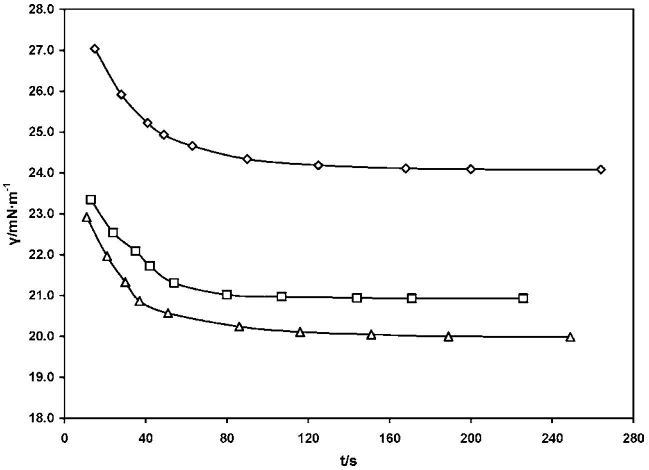

Figure 2. Interfacial tension of the system as a function of drop formation time for different samples: ◇, DTMAC, $c_t = 480.00 \cdot 10^{-6}$ mol·L^{-1}; □, Triton, $c_t = 60.00 \cdot 10^{-6}$ mol·L^{-1}; Δ, α = 0.1, $c_t = 360.00 \cdot 10^{-6}$ mol·L^{-1}.

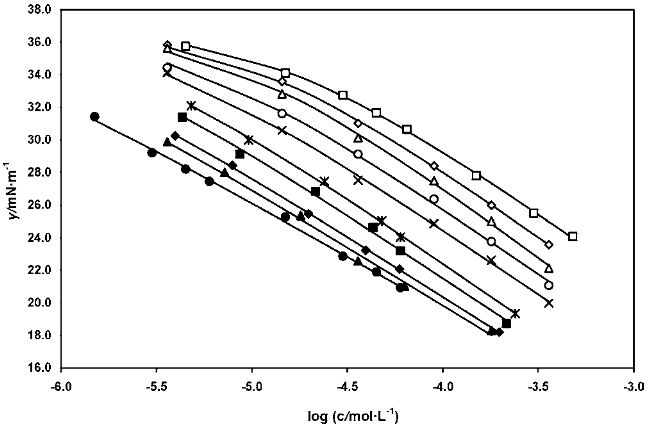

Figure 3. Interfacial tension of toluene + water versus log(c) of DTMAC, Triton, and their mixtures with different Triton bulk mole fractions in the bulk phases. The symbols are experimental: □, DTMAC; ◇, α = 0.005; Δ, α = 0.01; ○, α = 0.05; ×, α = 0.1; ∗, α = 0.2; ■, α = 0.4; ◆, α = 0.6; ▲, α = 0.8; ■, Triton; solid lines, fitting.

Presented in Figure 3, the interfacial tension data obtained for individual and for mixtures of investigated surfactants show a reduction in interfacial tension with the bulk concentration, significantly effective at low amounts, and of course, the ability of Triton to reduce the interfacial tension is much more than that of DTMAC. Despite the one-eighth maximum used concentration of Triton, it has reduced the interfacial tension to amounts less than that of DTMAC. The significant influence of Triton as a nonionic surfactant may be attributed to the low water solubility of the long carbon chain and an aromatic group in its hydrophobic group, which leads this molecule to orientate effectively at the interface.

b. Individual Surfactants. The obtained data with individual surfactants (8 data points for each) were fitted according to the Szyskowski equation[13,26] by nonlinear regression

$$\gamma = \gamma_o - nRT\Gamma_m \ln(1 + K_L c) \qquad (4)$$

where γ_o is the interfacial tension for clean chemical systems ($c = 0$) and Γ_m and K_L are the maximum interfacial concentra-

Table 2. Interfacial Tension Parameters of Maximum Surface Concentration, Γ_m, Langmuir Equilibrium Adsorption Constant, K_L, Gibbs Free Energy of Adsorption, $-\Delta G_{ads}$, Coefficients of Determination, R^2, and Area Occupied by the Surfactant Molecules, A_m, Values (at 25.0 °C)

	$10^6 \cdot \Gamma_m$	$10^{-7} \cdot K_L$		$10^{17} \cdot A_m$	$-\Delta G_{ads}$
compound	$mol \cdot m^{-2}$	$L \cdot mol^{-1}$	R^2	m^2	$kJ \cdot mol^{-1}$
Triton X-100	1.162	0.4104	0.9991	0.143	37.75
DTMAC	0.722	0.0074	0.9996	0.230	27.80

tion (saturated interface) of the adsorbed compound and the Langmuir equilibrium adsorption constant, respectively. Also, *n* is the number of species consisting of an adsorbing surfactant at the interface. All the concentrations are in molarity scale. The minimum corresponding molecular area occupied by a molecule at the interface and the Gibbs free energy of adsorption can be estimated from the following equations[26]

$$A_m = \frac{1}{\Gamma_m N_{Av}} \tag{5}$$

$$\Delta G_{ads} = -RT \ln(K_L) \tag{6}$$

where N_{Av} is the Avogadro's number.

The interfacial tension parameters as well as the calculated minimum area occupied by each compound molecule at the interface are listed in Table 2. The difference between calculated values (eq 4) and experimental data was obtained in terms of the so-called coefficient of determination (R^2)

$$R^2 = 1 - \frac{\sum_{i=1}^{N} (\gamma_{cal,i} - \gamma_{exp,i})^2}{\sum_{i=1}^{N} (\bar{\gamma} - \gamma_{exp,i})^2} \tag{7}$$

where N, γ_{cal}, γ_{exp}, and $\bar{\gamma}$ are, respectively, the number of data used in the fit, the interfacial tension calculated by the model, the experimental interfacial tension, and the average of all the appropriate experimental values in the fit. The given R^2 values in Table 2 and the standard deviations about regression which are less than ± 0.19 and ± 0.11 $mN \cdot m^{-1}$ for Triton and DTMAC, respectively, show the usefulness of the Szyskowski equation. Figure 3 shows the agreement. Using Triton X-100 surfactant in the toluene + water system at 25.0 °C, Giribabu and Ghosh[27] have reported Γ_m and K_L values close to those reported in this work.

The maximum surface concentration of a compound is the highest interfacial concentration attainable and relates to the level of decrease in interfacial tension. The higher Γ_m value for Triton represents a lower attainable interfacial tension, which can be attributed to the adsorption effectiveness of the surfactant. The surface activity of an added surfactant can also be characterized by its adsorption tendency, which can be attributed to the Gibbs free energy of adsorption. Again, the higher absolute value of ΔG_{ads} reflects the greater adsorption tendency of the Triton surfactant. It is obviously related to its K_L value that is 2 orders of magnitude larger than that of DTMAC surfactant.

c. Mixture of Surfactants. Mixtures of surfactants have received much attention in theoretical and experimental studies. The theory of nonideal interactions in binary mixtures (NIBM) developed by Rosen et al.[28,29] is usually used to determine the composition of mixed adsorbed layers and also the molecular interaction parameters. The variation of equilibrium interfacial tension should be employed. On the basis of the two-dimensional gas approach, the mixed monolayer can be considered as a mixture that is composed of only the surfactants, irrespective of the molecules of bulk phases.

The chemical potential of each surfactant at the interface and in the bulk of water phase can be expressed as

$$\mu_i = \mu_i^0 + RT \ln f_i x_i \qquad i = 1,2 \tag{8}$$

$$\mu_{i,w} = \mu_{i,w}^0 + RT \ln f_{i,w} c_{i,w} \qquad i = 1,2 \tag{9}$$

where μ_i is the chemical potential of surfactant 1 or 2 in the mixture at the interface; μ_i^0 is the standard chemical potential at the interface with ideal behavior which is a function of the interfacial pressure, $\Pi = \gamma_o - \gamma$; f_i is the activity coefficient of either surfactant at the interface; x_i is the mole fraction of either surfactant in the mixture at the interface; $\mu_{i,w}$ is the chemical potential of either surfactant in the bulk water phase; $\mu_{i,w}^0$ is the standard chemical potential of either surfactant in the water phase with the standard state of 1 molar and behaving ideally; $f_{i,w}$ is the activity coefficient of either surfactant in the water phase; and $c_{i,w}$ is the concentration of either surfactant in the water phase on the molarity scale.

When equilibrium is reached, the chemical potentials of each surfactant in the mixture at the interface and in the bulk phases are equal. From this equality, and when the concentration of surfactants in the bulk phases is low, the following equations, appropriate to either of the surfactants, can be obtained

$$\alpha c_{12} = x f_1 c_1^0 \tag{10}$$

$$(1 - \alpha) c_{12} = (1 - x) f_2 c_2^0 \tag{11}$$

where x is the mole fraction of surfactant 1 (Triton) in the mixture of surfactants in the mixed interface monolayer (on a surfactant-only basis); α is the molar fraction of surfactant 1 in the bulk solution; c_1^0, c_2^0, and c_{12} are the total bulk (in the two phases) molar concentration of compounds 1 and 2 and their mixture, respectively, to give a specified equilibrium interfacial tension. f_1 and f_2 are the activity coefficients of individual adsorbed compounds 1 and 2 in the mixed adsorbed monolayer between the organic−aqueous phases. The activity coefficients can be obtained from the second term of the Margules expansions (the first term being equal to zero)

$$f_1 = \exp\{\beta(1 - x)^2\} \tag{12}$$

$$f_2 = \exp\{\beta x^2\} \tag{13}$$

where β is the parameter of molecular interaction between the two compounds in the mixed adsorption monolayer, relative to the self-interaction of the compounds under the same conditions before mixing, given by the relationship

$$\beta = \frac{\ln(\alpha c_{12} / x c_1^0)}{(1 - x)^2} \tag{14}$$

Table 3. Values of Interfacial Mole Fraction of Triton, x, and Molecular Interaction Parameter, β, for Different Mixtures

α	γ / $\text{mN}\cdot\text{m}^{-1}$	x	β
0.005	24.0	0.246	−2.063
	26.0	0.248	−1.853
	28.0	0.250	−1.650
	30.0	0.252	−1.460
0.01	24.0	0.346	−2.732
	26.0	0.350	−2.419
	28.0	0.353	−2.120
	30.0	0.357	−1.836
0.05	24.0	0.527	−1.304
	26.0	0.549	−1.084
	28.0	0.574	−0.858
	30.0	0.601	−0.629
0.1	24.0	0.639	−1.270
	26.0	0.671	−0.995
	28.0	0.707	−0.696
	30.0	0.751	−0.368
0.2	24.0	0.710	−2.001
	26.0	0.747	−1.583
	28.0	0.792	−1.107
	30.0	0.849	−0.524

Negative β values roughly indicate attractive interactions, and positive values indicate repulsive interactions between the adsorbed molecules.

The mole fraction of the adsorbed compounds in the mixed adsorbed monolayer at the hydrocarbon−water interface can be estimated by this theory, using the relationship

$$\frac{x^2 \ln(\alpha c_{12}/c_1^0 x)}{(1 - x)^2 \ln[(1 - \alpha)c_{12}/c_2^0(1 - x)]} = 1 \qquad (15)$$

To use the above equations, the phases' volume ratio should be constant, and the partition coefficient of each surfactant remains constant when both of them are present. It is the case for low concentration of compounds that is normally used.[28] Equations 14 and 15 have been extensively used for nonionic−nonionic and nonionic−ionic surfactant mixtures.[6]

For a specified interfacial tension, the appropriate c_1^0, c_2^0, and c_{12} values can be determined from experimental interfacial tension isotherms of surfactants 1, 2, and their mixture at a certain α value, respectively. Having these parameters, the exact value of x was calculated from eq 15 by the numerical iteration method. Angarska et al.[4] have used a similar procedure.

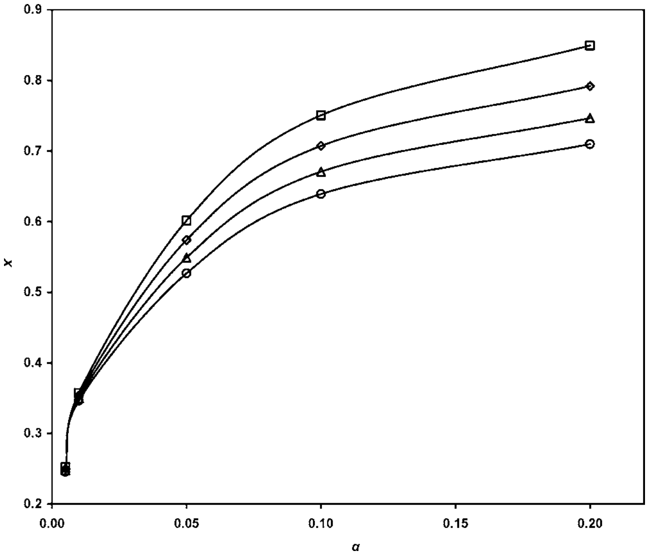

Figure 4. Interfacial mole fraction of Triton (x) versus its bulk mole fraction (α)for different interfacial tensions: □, $\gamma = 30.0\ \text{mN}\cdot\text{m}^{-1}$; ◇, $\gamma = 28.0\ \text{mN}\cdot\text{m}^{-1}$; Δ, $\gamma = 26.0\ \text{mN}\cdot\text{m}^{-1}$; ○, $\gamma = 24.0\ \text{mN}\cdot\text{m}^{-1}$.

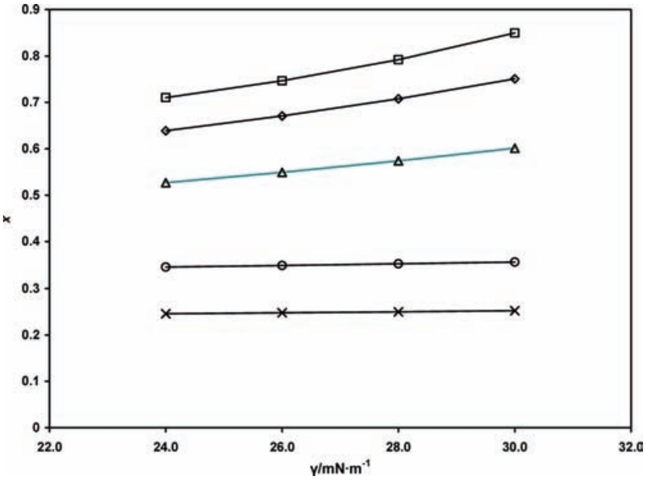

Figure 5. Interfacial mole fraction of Triton (x) versus interfacial tension for different bulk mole fractions: □, α = 0.2; ◇, α = 0.05; ○, α = 0.01; ×, α = 0.005.

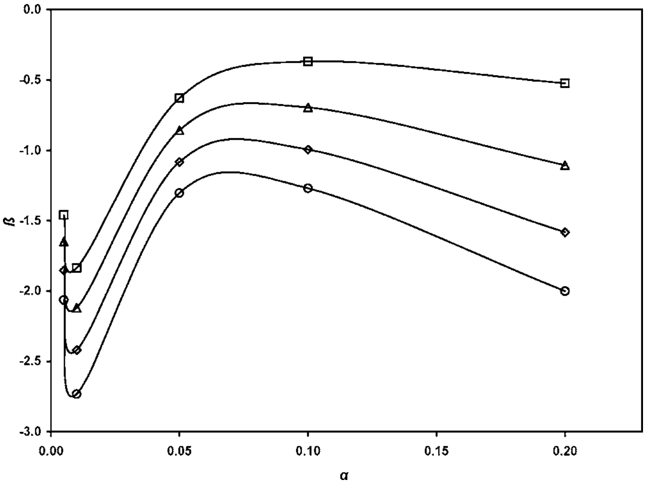

Figure 6. Interaction parameter between surfactants at the interface (β) versus Triton bulk mole fraction (α) for different interfacial tensions: □, $\gamma = 30.0\ \text{mN}\cdot\text{m}^{-1}$; Δ, $\gamma = 28.0\ \text{mN}\cdot\text{m}^{-1}$; ◇, $\gamma = 26.0\ \text{mN}\cdot\text{m}^{-1}$; ○, $\gamma = 24.0\ \text{mN}\cdot\text{m}^{-1}$.

As presented in Figure 3, the isotherms with mixed surfactants remain within the limits of two individual compounds when the bulk mole fraction, α, varies; however, low contributions of DTMAC in bulk composition do not lead to a significant reduction in strong influence of Triton. The higher absolute adsorption energy ($-\Delta G_{\text{ads}}$) relevant to Triton seems to cause a significant contribution in the reduction of interfacial tension by this surfactant, e.g., the interfacial tension isotherms become close to the DTMAC isotherm when bulk mole fractions of Triton find values less than only 0.01.

It is noteworthy that the mutual position of isotherms obtained for individual surfactants and for their mixture shows that no synergism in interfacial tension reduction (providing a total mixed compound concentration lower than that required of either compound by itself to attain a given interfacial tension) is relevant.

The obtained interfacial tension isotherms for systems with individual compounds and for mixed systems with different bulk mole fractions enable the estimation of the values of parameters.

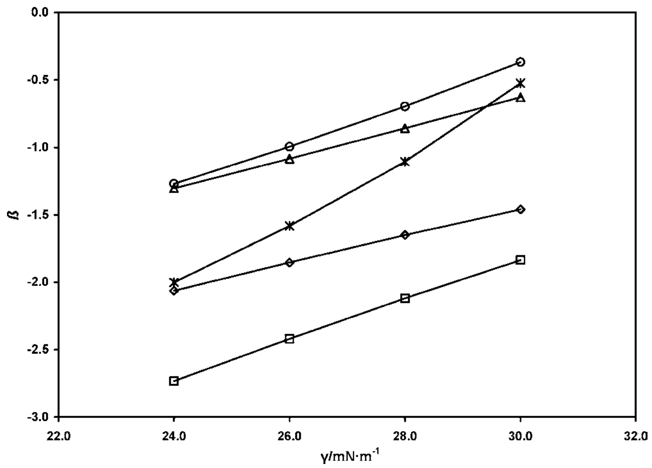

Figure 7. Interaction parameter between surfactants at the interface (β) versus interfacial tension for different Triton bulk mole fraction: ○, α = 0.1; Δ, α = 0.05; ∗, α = 0.2; ◇, α = 0.005; □, α = 0.01.

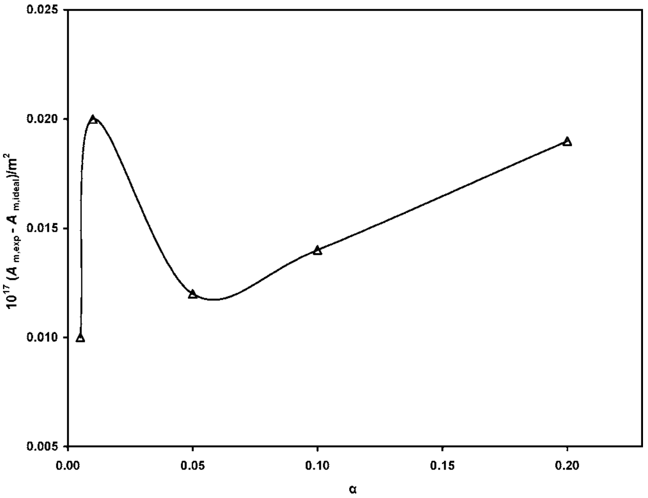

Figure 8. Absolute difference between experimental and ideal areas per molecule, versus Triton bulk mole fraction (α).

Table 4. Experimental, $A_{\mathrm{m,exp}}$, and Ideal, $A_{\mathrm{m,ideal}}$, Molecular Area for Different Bulk Compositions of Triton

α	$\bar{x}$	n	$10^6 \cdot \Gamma_\mathrm{m}$ mol·m^{-2}	$10^{17} \cdot A_{\mathrm{m,exp}}$ m^2	$10^{17} \cdot A_{\mathrm{m,ideal}}$ m^2	$10^{17} \cdot (A_{\mathrm{m,exp}} - A_{\mathrm{m,ideal}})$ m^2
0.005	0.249	1.751	0.838	0.198	0.208	−0.010
0.01	0.352	1.648	0.926	0.179	0.199	−0.020
0.05	0.563	1.437	0.980	0.169	0.181	−0.012
0.1	0.692	1.308	1.062	0.156	0.170	−0.014
0.2	0.775	1.225	1.158	0.143	0.162	−0.019

The obtained values of surface mole fraction of Triton, x, from eq 15 (based on the obtained c_1^0, c_2^0, and c_{12} values from Figure 3) and also molecular interaction parameter, β, from eq 14, for the five different applied bulk mole fractions are listed in Table 3. The four considered γ values [(24.0, 26.0, 28.0, and 30.0) mN·m^{-1}] are consistent with the range of variations for all the individuals and mixtures of compounds.

It has to be noted that investigations for the above-mentioned purposes showed that Triton bulk mole fractions more than 0.2 are not consistent with the NIBM theory (even at low bulk concentrations). This matter can be argued with the significant difference in tendency and effectiveness of the surfactants to be adsorbed at the interface and forming surface monolayer. Bulk mole fractions of Triton more than 0.2 provide interface mole fractions quite close to 1 which, in turn, give very high (tending infinite) interaction parameters according to eq 14 and not consistent with NIBM theory as this subject is confirmed by Janczuk et al.[30] Bulk mole fractions of Triton less than 0.2 can provide adequate contribution of both the surfactants to be adsorbed at the interface.

Within the range of investigated interfacial tension and with the bulk mole fractions of 0.005 to 0.2, the range of Triton mole fraction at the toluene + water interface is between 0.246 and 0.849. The presented data show clearly that the composition of Triton at the mixed adsorbed monolayer is much more than the composition of the bulk aqueous phase, and it is the dominant adsorbed component for bulk mole fractions equal to and more than 0.05. The higher adsorption effectiveness and tendency lead to favor the Triton molecules to find a higher mole fraction ratio at the interface. As is represented by Figure 4, the interface composition rises rapidly with the bulk composition and then finds mild variation.

Previous investigations in the rate of mass transfer for the liquid−liquid extraction process report the stronger retarding effect of Triton for either of the toluene + acetone + water[11] and carbon tetrachloride + acetic acid + water[10] chemical systems. It can therefore be concluded that the resistance to mass transfer of a solute to be extracted from either phase (toluene or water) increases significantly with addition of a very low amount of Triton to the medium. This matter also agrees with the mass transfer variations in the above-mentioned references. On the other hand, as was given in Table 2, the estimated area allocated to a DTMAC molecule (0.230·10^{-17} m^2) is significantly more than that of a Triton molecule (0.143·10^{-17} m^2) which can lead to free spaces, favoring the solute to be transferred through the interface. Of course, the interaction between the surfactants and the solute can impose another influence. To assess this subject, further mass transfer investigations are required in the presence of surfactant mixtures.

The results also show (Figure 5) that the value of x almost remains constant with interfacial tension at low bulk mole fractions of 0.005 and 0.01; however, it increases significantly as the bulk mole fraction exceeds 0.05. This subject is a consequence of the ratios of c_{12}/c_1^0 and c_{12}/c_2^0, obtained from Figure 3, i.e., the trend of curves versus surfactants concentration. Prochaska[31] and Staszak[32] have reported similar variations due to the presence of binary extractant and modifier compounds in octane−water systems, relevant to hydrometallurgical practice.

The obtained negative β values for all the cases indicate that the interactions between the two surfactants are more attractive or less repulsive. In other words, it can be said that an interaction more attractive or less repulsive than the self-interaction of the two surfactants before mixing is dominant.

The variation of β versus the bulk mole fraction, α, and versus the interfacial tension is presented in Figures 6 and 7, respectively. The interaction parameter varies with different trends in the investigated range of α. As it is apparent, and given in Table 3, the maximum attractive interaction between the compounds belongs to the Triton bulk mole fraction of about 0.01 with the appropriate interfacial mole fraction of about 0.35. This composition is equivalent with a ratio of 1:2 of Triton and DTMAC molecules, respectively, which can lead to a maximum dilution effect and overcoming the repulsion between DTMAC molecules, while the minimum absolute interactions are appropriate for bulk mole fractions between 0.05 and 0.1. With respect to the interface composition in this region, it can be said that the repulsion interaction influences effectively to weaken the dominant attraction between surfactants. Higher bulk

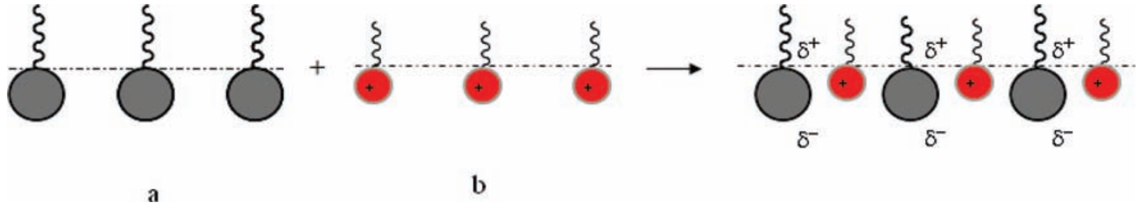

Figure 9. Schematic presentation of interactions between Triton (a) and DTMAC (b) molecules at the interface.

compositions of Triton lead to much lower DTMAC interface composition and consequently lower electrostatic repulsion. From these variations, it can be inferred that the structures of the adsorbed layer, formed under different bulk mole fractions, are quite different.

In this regard, further investigations were performed by estimating the allocated area for the adsorbed molecules at the interface. For this purpose, the Gibbs adsorption equation

$$\Gamma = -\frac{1}{2.303nRT}\left(\frac{d\gamma}{d\log c}\right) \qquad (16)$$

was used, in which Γ is the equilibrium surface concentration and n is the number of species that should be calculated from[5]

$$n = n_1\bar{x} + n_2(1 - \bar{x}) \qquad (17)$$

where n_1 and n_2 are the number of species of the nonionic surfactant Triton (equals 1) and of the ionic surfactant DTMAC (equals 2), respectively. Also, $\bar{x}$ is the mean interfacial composition appropriate to interfacial tensions of a specified α value. To obtain the Γ_m values, $(d\gamma/d\log c)$ should be the maximum slope in the γ versus $\log c$ plot.

The above experimentally obtained molecular area, $A_{m,exp}$, can be compared with the corresponding ideal mixing area, $A_{m,ideal}$, calculated from equation[5,22]

$$A_{m,ideal} = \bar{x}A_{m,1} + (1 - \bar{x})A_{m,2} \qquad (18)$$

where $A_{m,1}$ and $A_{m,2}$ are the appropriate molecular area of individual surfactants 1 and 2. The results presented in Table 4 give the experimental and ideal calculated molecular area as well as the difference between them that is a criterion of deviation from the ideality. The values of $A_{m,ideal}$ are within the individual surfactant values, presented in Table 2.

As is obvious in Table 4, the values of $A_{m,exp}$ are less than $A_{m,ideal}$, which implies that in agreement with the negative β values a contraction upon mixing is appropriate. Meanwhile, the variations of absolute $A_{m,exp} - A_{m,ideal}$ versus the bulk mole fraction, α, as indicated in Figure 8 are contrary to the variation of β (Figure 6) which is consistent, due to the point that a higher absolute β parameter is corresponding to have closer location of molecules and giving a higher absolute difference of experimental and ideal area per molecule. As expected, the highest difference is for the bulk mole fraction of 0.01, with a difference of $0.020 \cdot 10^{-17}$ m^2.

The above-mentioned variations can be argued, considering the chemical structure of surfactants (Figure 1). Before mixing, the ionic surfactant DTMAC has a strong electrostatic self-repulsion on its hydrophilic headgroup; the nonionic surfactant, Triton, on the other hand, has a steric self-repulsion. Both of these mutual repulsions are weakened in mixture by a dilution effect, presumably due to ion−dipole attractive interaction. van der Waals attractive interaction between the hydrophobic groups of surfactants can also help a rather closeness of the molecules. Figure 9 shows a proposed schematic arrangement of interface orientation of the surfactant molecules. Zhou and Rosen[5] have given alternative interactions between different kinds of surfactants.

Conclusions

Adding bulk surfactant concentrations less than $6.00 \cdot 10^{-5}$ mol·L^{-1} of Triton X-100 and $4.80 \cdot 10^{-4}$ mol·L^{-1} of DTMAC (much less than their aqueous CMC values) can individually reduce the interfacial tension of the well-known chemical system of toluene + water significantly. With the aim of obtaining the adsorption parameters for individual compounds, the Szyszkowski equation predicts the appropriate isotherms quite well.

The influence of DTMAC in lowering interfacial tension can be enhanced by adding Triton with bulk mole fractions even less than 0.01. This serious influence can be attributed to the higher Triton absolute energy of adsorption and its interface effectiveness.

All the bulk mole fractions isotherms lie within the limits of individual surfactants (no synergism); however, only mole fractions less than 0.2 provide results, which agree with the NIBM theory. Within this range, the estimated interfacial composition of Triton is several times that in bulk and rises rapidly as the bulk mole fraction increases. This matter agrees with the previous works indicating rapid reduction with the low amounts of Triton.

The attractive interaction in the mixed adsorbed monolayer is strongly dependent on the bulk composition. Possible formation of ion−dipole attractive interactions can provide this sort of variation. In this regard, the bulk mole fractions between 0.05 and 0.1 of Triton are appropriate for the minimum attraction of the compounds at the interface. Moreover, a consistent lower experimental area per molecule than the ideal estimated value and an inverse variation of attraction interaction, compared with absolute difference of experimental and ideal area per adsorbed molecule, are obvious.

Supporting Information Available:

Table SM1: drop volume, v, density of phases, ratio of $r/v^{1/3}$, drop weight method correction constant, $f(r/v^{1/3})$, and drop formation time values. Table SM2: flow rate, drop formation time, drop volume, density of phases, correction constant, and interfacial tension values for equilibrium conditions achievement (appropriate to Figure 2). This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review April 1, 2010. Accepted June 14, 2010.

JE100322T