

# Interfacial Behavior of Aqueous Solutions of Cetyltrimethylammonium Bromide (CTAB), Additives and Their Mixtures: The Experimental and Modeling Study

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**ABSTRACT:** *In the present investigation, firstly, the surface tension measurements were conducted for aqueous solutions of cetyltrimethylammonium bromide, acetonitrile, and tetrahydrofuran by using a pendant drop apparatus at the temperature of 298.15 K and ambient pressure. Then a thermodynamic model was used and successfully reproduced the surface tension values. The percent of the average absolute deviation for surface tension was 0.667. The surface tensions of mixed aqueous solutions of (cetyltrimethylammonium+additives) were measured at various concentrations. Then, the values of critical micelle concentrations were measured based on surface tension and conductivity. The percent of the average absolute deviation of the thermodynamic model was 5.05, proving that the model successfully predicts the surface tension for aqueous mixed solutions of (cetyltrimethylammonium+additives). The presence of additives decreases the surface coverage of cetyltrimethylammonium and increases the critical micelle concentration values.*

**KEYWORDS:** *Cetyltrimethylammonium; Acetonitrile; Tetrahydrofuran; Surface tension; Critical micelle concentration.*

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1021-9986/2022/2/555-565

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## INTRODUCTION

In recent years, surfactant research attracted much attention in different realms such as petroleum oil recovery, pollution control, foaming and detergency, and analytical chemistry. As a consequence, investigations are being conducted to develop surfactants with better interfacial and adsorption properties. The application of a single surfactant is not enough to provide all the required properties. One method of enhancing the properties of a surfactant solution is to use an appropriate additive. As an example, various quantities of alcohol can significantly change the performance of a micellar solution. Such strategies can be beneficial from an industrial point of view because they result in reducing operational costs and environmental disadvantages. The mixture of additive-surfactant can be applied to foods, cosmetics, mineral processing, paints, coating, polymer synthesis, adhesives, and pharmaceutical products. Therefore, the physicochemical properties of such mixed solutions have attracted much attention in the realm of amphiphiles [1-8].

The most important property of a surfactant is its ability to form a micelle. The balance of hydrophobic and hydrophilic forces governs micellization. After a certain concentration, surfactants form micelle and this concentration is defined as Critical Micelle Concentration (CMC). In addition, additives affect the micellization behavior of surfactants through non-chemical interactions. Characterization of a mixed surfactant system or (surfactant+additive) system is possible through Critical Micelle Concentration (CMC) which has been measured based on the surface tension. More precisely, the deviation from the ideal state is used to determine the properties of (surfactant+additive) aqueous solutions. This non-ideality can be described by using an interaction parameter. Therefore, knowing how these additives interact with surfactants is important. Using an appropriate thermodynamic model enables a researcher to describe the behavior of such systems according to the interactions between two surfactants or the surfactant and the additive [9-11].

In most cases, common additives used in combination with surfactants involve urea, sugar, salt, and polymers (both neutral and charged). Hydrophilic neutral additives affect the micellization of surfactants in some non-chemical way. Among various mixed systems, the mixtures of an anionic surfactant and an additive have attracted much attention due to their wide application,

especially in the realm of detergency. Surprisingly, studies on surfactant aggregation in the presence of acetonitrile and tetrahydrofuran (THF) show that it is still poorly understood. This lacuna has convinced us in studying the interfacial and micellization behavior and subsequent evaluation of associated parameters of cationic surfactant CTAB in the presence of acetonitrile and tetrahydrofuran (THF) systems. It is believed that such studies would shed new light on the understanding of the micellization behavior of CTAB for practical formulation in water-acetonitrile/tetrahydrofuran (THF) mixtures.

Therefore, the present study aims to determine the effect of additives (including acetonitrile and tetrahydrofuran) on the interfacial properties of the aqueous solutions of cetyltrimethylammonium (CTAB). To achieve this aim, firstly, the surface tension of the applied aqueous solutions of individual substances is measured by using a pendant drop apparatus. Then a thermodynamic model based on the equality of chemical potentials is applied to the surface tensions of aqueous solutions. These measurements have been carried out for the aqueous mixtures of (CTAB+additives). The experimental surface tensions have been used to measure the Critical Micelle Concentrations (CMCs). Also, Critical Micelle Concentrations (CMC) of (CTAB+ additives) were determined by measurement of conductivity and compared with CMCs obtained by measurement of surface tension. For the first time, by using the thermodynamic model, the surface coverage has been computed for the aqueous solution of (CTAB+additives). The effect of the applied additives on the interfacial behavior of CTAB has been discussed.

## EXPERIMENTAL SECTION

### Materials

CTAB (cetyltrimethylammonium) with a purity of 99% was purchased from Merck Company, Germany. Also, acetonitrile and tetrahydrofuran with a purity of 99% were from Merck, Germany. Distilled water was used to prepare the solutions for all the experiments. A digital electronic balance with the uncertainty of  $\pm 0.1$  mg was used to weigh the materials. The densities of the aqueous solutions were measured with a glass pycnometer.

### Apparatus

A pendant drop apparatus built in our laboratory was used to measure the surface tensions of the aqueous solutions.

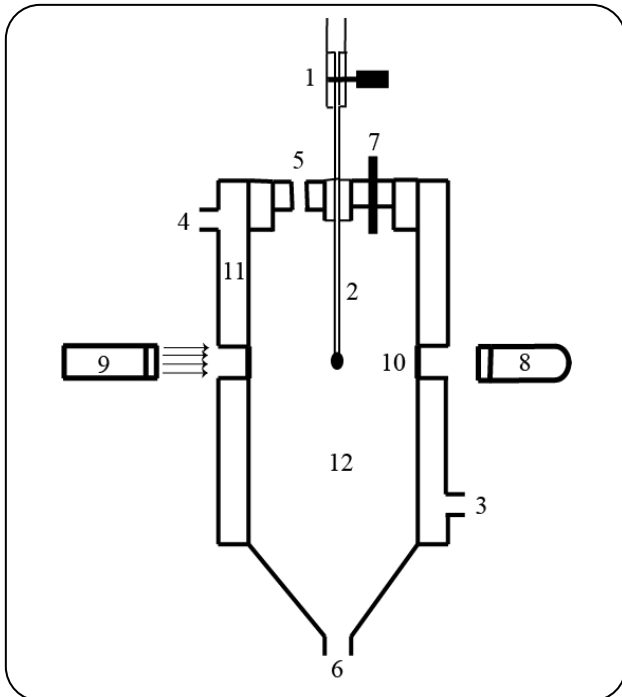


Fig. 1: The schematic of the apparatus for measuring the surface tension of surfactant solutions (pendant drop), 1. Needle valve; 2. Glass capillary tube; 3. Inlet of the jacket; 4. Outlet of the jacket; 5. Inlet of the air; 6. To the vacuum; 7. Thermometer; 8. Digital Camera; 9. Light source; 10. Sight glass; 11. Jacket of the cell; 12. Cell.

Fig. 1 shows the schematic of the applied pendant drop apparatus. All experiments were conducted in a cylindrical glass cell with a total volume of 500 mL. Two sight glasses of the cell allow a user to observe the droplet from a horizontal axis. This set-up has a glass capillary tube to create a hanging drop. The inner and outer diameters of the applied capillary tube were 1.2 mm and 1.6 mm, respectively. The sample of each aqueous solution was injected into the cell with a needle valve. A pendant drop was formed at the tip of the capillary tube. This system can operate at the ambient pressure and temperature range of (275.15-373.15) K. A PT100 thermometer (Pro-Temp Controls, Santa Ana, California, United States) with an accuracy of  $\pm 0.1$  K was applied to measure temperature. To capture the images of the drops and measure the surface tension of each aqueous solution, a digital camera was utilized. The applied camera was connected to a personal computer. The uncertainty of the measurements for surface tension was  $\pm 0.5$  mN/m. Also, a conductivity probe (Con110, Lovibond, Germany) was used to measure the conductivity of aqueous solutions.

### Experimental procedure

Prior to any measurements, the overall apparatus was washed with distilled water three times. Then the compressed air was used to dry the cell and its connections. A solution with a specified concentration was made and injected into the pendant drop cell by using a needle valve and capillary tube. A vertical pendant drop was formed with a capillary tube. The images of the drop were taken during the experiment by means of a digital camera. Then the droplet dimensions were measured. The surface tension was calculated by using Eq. (1) [12].

$$\gamma = \frac{\Delta \rho d_e^2 g}{H} \quad (1)$$

in which  $\Delta \rho$  shows the difference in the density between gas and liquid phases,  $g$  indicates the gravitational constant.  $d_e$  is the maximum diameter of the liquid droplet and  $d_s$  belongs to the diameter of the liquid droplet measured at a distance of  $d_e$  from the bottom of the droplet. The parameter  $(1/H)$  is computed from [13] in terms of the

$$\left[ \frac{1}{H} = f(d_s/d_e) \right]$$

### MODEL DESCRIPTION

In this section, only the required equations of the model have been mentioned. A detailed description of the model can be found in [14,15]. When chemical potentials in the liquid phase and interface are set equal, the surface tension model can be derived. The chemical potential of a component in the liquid phase is calculated through Eq. (2).

$$\mu_i^\alpha = \mu_i^{0\alpha} + R T \ln(f_i^\alpha x_i^\alpha) \quad (2)$$

Where  $\mu_i$  indicates the chemical potential of component  $i$ ,  $\mu_i^0$  shows the standard chemical potential,  $f$  represents the activity coefficient,  $x_i$  shows the mole fraction of component  $i$  in the liquid phase,  $R$  is the universal gas constant (8.314 J/mol K), and  $T$  shows the absolute temperature. The superscript  $\alpha$  belongs to the liquid phase.

The interfacial chemical potential is stated as follows:

$$\mu_i^\sigma = \mu_i^{0\sigma} + R T \ln(f_i^\sigma x_i^\sigma) - \gamma \omega_i \quad (3)$$

where  $\gamma$  denotes the surface tension of the aqueous solution.  $\omega$  shows the partial molar surface area, and the superscript  $\sigma$  belongs to the surface layer.

According to the thermodynamic equilibrium, the chemical potentials of component  $i$  in the bulk and the surface layer is the same. Hence, the following equation exists:

$$\mu_i^\alpha = \mu_i^\sigma \quad (4)$$

A solvent ( $i=0$ ) at the standard state is considered a pure solvent. This assumption leads to  $x_i^\alpha = x_i^\sigma = 1$ ,  $f_i^\alpha = f_i^\sigma = 1$ , and  $\gamma = \gamma_0$ .

Using the above considerations and a combination of the Eqs. (2)-(4), Eq. (5) can be derived as follows:

$$\mu_0^{0\sigma} - \gamma_0 \omega_0 = \mu_0^{0\alpha} \quad (5)$$

The assumption of the infinitely dilute solution ( $x_i^\alpha \rightarrow 0$ ) has been used for the standard state of the solute ( $i=1$ ); so  $f_i^\alpha = f_i^\sigma = 1$ ,  $\gamma = \gamma_0$ .

Using Eqs. (2)-(5), the following equations are derived [14,15].

$$R T \ln (f_0^\sigma x_0^\sigma) = -(\gamma_0 - \gamma) \omega_0 \quad (6)$$

$$\ln \frac{f_1^\sigma x_1^\sigma / f_{10}^\sigma}{K_1 f_1^\alpha x_1^\alpha} = -\frac{1}{R T} (\gamma_0 - \gamma) \omega_1 \quad (7)$$

in which  $K_1 = \left( x_1^\sigma / x_1^\alpha \right) \Big|_{x_1^\alpha \rightarrow 0}$  shows the distribution coefficient at infinite dilution of solute.  $\pi = \gamma_0 - \gamma$  shows the surface pressure, and  $f_{10}$  states infinite dilution. Eqs. (8) and (9) have been obtained from Eqs. (6) and (7):

$$\pi = -\frac{R T}{\omega_0} (\ln x_0^\sigma + \ln f_0^\sigma) \quad (8)$$

$$\ln \frac{f_1^\sigma x_1^\sigma / f_{10}^\sigma}{K_1 f_1^\alpha x_1^\alpha} = \frac{\omega_1}{\omega_0} (\ln x_0^\sigma + \ln f_0^\sigma) \quad (9)$$

The interfacial mole fraction and surface coverage can be related by using Eq. (10).

$$x_k^\sigma = \frac{\theta_k}{n_k \sum_{i \geq 0} (\theta_i / n_i)}, n_i = \omega_i / \omega_0, \theta_k = \Gamma_k \omega_k \quad (10)$$

In the above equation,  $\theta$  and  $\Gamma$  show the surface coverage and surface excess concentration, respectively.

$\omega_s$  and  $\omega_b$  belong to the molar surface area of the surfactant and solvent, respectively.

For the aqueous solution of an individual surfactant, one can use the following equations for the activity coefficients.

$$\ln f_0^\sigma = \ln \left[ 1 - \left( 1 - \frac{1}{n_1} \right) \theta_1 \right] + \left( 1 - \frac{1}{n_1} \right) \theta_1 + a \theta_1^2 \quad (11)$$

$$\ln f_1^\sigma = \ln (n_1 + (1 - n_1) \theta_1) + (1 - n_1)(1 - \theta_1) + a n_1 \theta_1^2 \quad (12)$$

$$\ln f_{10}^\sigma = \ln n_1 + (1 - n_1) + a n_1 \quad (13)$$

in which  $a$  indicates the interaction parameter. Eqs. (11)-(13) are replaced into Eqs. (8) and (9) with  $f_1^\alpha = 1$ . Therefore, the equation of state and adsorption isotherm have been derived as follows:

$$\pi = -\frac{R T}{\omega_0} \left( \ln (1 - \theta_1) + \left( 1 - \frac{1}{n_1} \right) \theta_1 + a \theta_1^2 \right) \quad (14)$$

$$b c = \frac{\theta_1}{n_1 (1 - \theta_1)^{n_1}} \exp(-2 a n_1 \theta_1) \quad (15)$$

In Eqs. (14) and (15),  $c$  is the concentration in the liquid phase,  $b$  shows the surface-to-solution distribution coefficient ( $b c = K_1 x_1^\alpha$ ).  $\omega_b$  shows the molar surface area of the water. In this study, the following equation [16,17] has been applied to the surface molar area.

$$\omega_0 = (1.021 \times 10^8) V_c^{6/15} V_b^{4/15} \quad (16)$$

where  $V_b$  and  $V_c$  indicate the molar volume and the critical molar volume of the pure water, respectively. They are in  $\text{cm}^3/\text{mol}$  and  $\omega_b$  is in  $\text{cm}^2/\text{mol}$ . In Eqs. (14) and (15),  $R$ ,  $T$ ,  $\omega_b$ , and  $c$  are the known parameters.  $a$ ,  $b$ , and  $\omega_1$  are adjustable parameters that can be determined by minimizing mean absolute deviations of the surface tension. The average absolute deviation of the surface tension is computed by Eq. (17).

$$A A D_\gamma = \frac{1}{N} \sum_{i=1}^N \left| \frac{\gamma_i^{\text{exp.}} - \gamma_i^{\text{calc.}}}{\gamma_i^{\text{exp.}}} \right| \times 100 \quad (17)$$

Where  $N$  is the number of experimental data.  $\pi$  and  $\theta$  are unknown parameters of the model calculated by the simultaneous solution of Eqs. (14) and (15).

The present model for aqueous solutions of (surfactant + additive) is expressed as follows:

$$\pi = -\frac{RT}{\omega_0} \left[ \ln(1 - \theta_1 - \theta_2) + \theta_1 \left( 1 - \frac{1}{n_1} \right) + \right. \quad (18)$$

$$\left. \theta_2 \left( 1 - \frac{1}{n_2} \right) + a_1 \theta_1^2 + a_2 \theta_2^2 + 2a_{12} \theta_1 \theta_2 \right]$$

$$b_1 c_1 = \frac{\theta_1}{(1 - \theta_1 - \theta_2)^{n_1}} \exp(-2a_1 \theta_1 - 2a_{12} \theta_2) \times \quad (19)$$

$$\exp\left((1 - n_1)(a_1 \theta_1^2 + a_2 \theta_2^2 + 2a_{12} \theta_1 \theta_2)\right)$$

$$b_2 c_2 = \frac{\theta_2}{(1 - \theta_1 - \theta_2)^{n_2}} \exp(-2a_2 \theta_2 - 2a_{12} \theta_1) \times \quad (20)$$

$$\exp\left((1 - n_2)(a_1 \theta_1^2 + a_2 \theta_2^2 + 2a_{12} \theta_1 \theta_2)\right)$$

The value of  $a_{12}$  can be considered as follows [15]:

$$a_{12} = \frac{a_1 + a_2}{2} \quad (21)$$

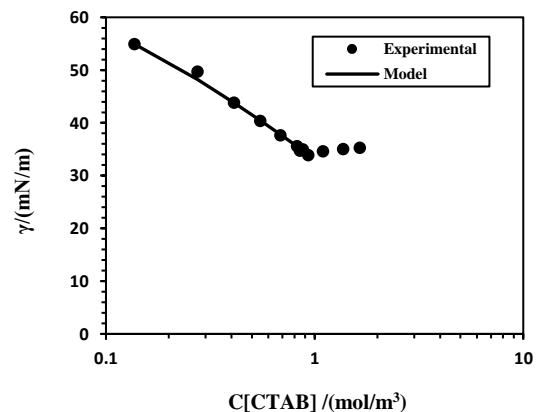
In Eqs. (18)-(20),  $\theta_1$ ,  $\theta_2$ , and  $\pi$  are unknown parameters calculated through the simultaneous solution of Eqs. (18)-(20).

## RESULTS AND DISCUSSION

Since all elements of this research are based on surface tension measurements, the measurements have to be validated to validate this research. The reliability of the surface tension measurements was tested and confirmed in previous studies [18,19]. Similar to previous studies [18,19], all experiments were done at a temperature of 298.15 K and ambient pressure. The surface tension measurements of an aqueous solution of CTAB, acetonitrile, and tetrahydrofuran were carried out at different concentrations. Each experiment was performed three times to ensure that all measurements are consistent. Therefore, each experimental surface tension has been considered as an average of three measurements. Table 1 presents the experimental surface tensions. Fig. 2 shows the surface tension of the aqueous solution of CTAB in terms of concentration. Similar to the other cationic surfactants, the surface tension decreases as the concentration of CTAB increases until the concentration of CTAB reaches critical micelle concentration (CMC). When the concentration of CTAB reaches CMC, and micelles of CTAB can form.

**Table 1: Experimental and computed surface tensions for the aqueous solutions of CTAB, Acetonitrile, and Tetrahydrofuran at  $T = 298.15$  K and  $P = 1$  atm.**

C(mol/m <sup>3</sup> )	$\gamma_{\text{exp}}/(\text{mN/m})$	$\gamma_{\text{cal}}/(\text{mN/m})$
CTAB		
0.137	54.91	54.91
0.274	49.69	48.22
0.411	43.81	43.80
0.549	40.34	40.47
0.686	37.60	37.80
0.823	35.56	35.56
0.850	34.69	-
0.878	34.94	-
0.933	33.82	-
1.097	34.55	-
1.372	34.98	-
1.646	35.25	-
Acetonitrile		
3.654	68.13	68.48
12.180	67.46	67.46
24.360	66.83	66.78
36.541	66.58	66.36
48.721	66.28	66.05
60.901	66.13	65.79
73.081	65.51	65.59
85.262	65.41	65.41
97.442	65.29	65.25
109.622	65.00	65.11
121.802	64.79	64.98
Tetrahydrofuran		
6.934	68.86	67.43
13.868	67.59	66.33
20.802	67.04	65.62
27.736	65.76	65.09
34.670	64.67	64.67
41.605	63.92	64.31
55.473	63.09	63.73
69.341	63.01	63.27



**Fig. 2: Experimental and reproduced surface tensions for the aqueous solution of CTAB at the temperature of 298.15 K.**

**Table 2: The molar area, surface-to-solution distribution constant, and interactions for aqueous solutions of pure CTAB, Acetonitrile, and Tetrahydrofuran by using the model.**

Chemical	Parameter		
	$\omega / (10^3 \text{m}^2/\text{mol})$	$b / (\text{m}^3/\text{mol})$	$a$
CTAB	1.6705	12.824	-0.0844
Acetonitrile	7.762	0.9087	-0.6207
Tetrahydrofuran	7.0806	0.1371	0.1579

At concentrations higher than CMC, the surface tension of the aqueous solution of CTAB does not change because the interface is fully occupied by surfactant molecules and no more surfactant can be absorbed. Based on the surface tension measurements, the CMC of CTAB was  $0.823 \text{ mol/m}^3$ . This measured value is in good agreement with the previous studies [18,19].

Then a theoretical model was used to reproduce the surface tension of aqueous solutions of CTAB and additives, including acetonitrile and tetrahydrofuran. The applied model was according to the equality of chemical potentials in the liquid phase and the surface layer. The model is only applicable to concentrations lower than the critical micelle concentration. The fitting parameters of the present model, including  $a$ ,  $b$ , and  $\omega_l$  were regressed based on the surface tension data. Table 2 shows these three parameters for each pure substance. To compute  $\omega_b$ , Eq. (16) was used. Furthermore, to use Eq. (16) the values of  $V_b$  and  $V_c$  are  $18.069 \text{ cm}^3 \cdot \text{mol}^{-1}$  and  $57.1 \text{ cm}^3/\text{mol}$ , respectively [20].

When Eqs. (14) and (15) are used, and the surface pressure ( $\pi$ ) and surface coverage ( $\theta$ ) can be calculated. A good agreement with the experimental surface tensions exists, so the present model successfully reproduces changes in surface tension in terms of concentration. The overall value of  $AAD_\gamma$  was 0.667. Table 2 proves that the surface-to-solution distribution constants ( $b$ ) of the applied additives are much lower than the ones for CTAB. This shows that the additives do not show a high surface activity when compared with CTAB.

To study the influence of additives on the interfacial behavior of CTAB, the aqueous solutions of (CTAB +additives) were prepared. The concentration of additives was 10 wt%, 20 wt%, 30 wt%, and 40 wt%. Like the previous section, firstly, the surface tension of the prepared aqueous solutions is measured. Table 3 shows the experimental surface tension data.

Then the surface tension measurements were used to determine the CMC of the prepared mixed solutions. The measured CMC values have been reported in Table 4 and Table 5. The results in Table 4 and Table 5 show that the CMC of CTAB increases in the presence of the applied additives. Also, the CMC of CTAB increases when the percentage of additives increases. This can be interpreted as follows. Increasing the concentration of additives leads to increasing the hydrophobicity of the liquid phase. When a single surfactant is present in an aqueous solution, the hydrophobic tail group of this surfactant tends to adsorb at the surface layer. In the presence of an additive, due to an increase in the hydrophobicity of the aqueous solution, more hydrophobic tails of CTAB can stay in the liquid phase. On the other hand, the main driving force of micelle formation [21] is the influence of hydrophobicity due to the hydrophobic tail of surfactants. Therefore, the CMC of CTAB solution increases when it is used in the presence of additives.

Since the performance of the model was good in the previous section, the model was applied to the aqueous solutions of (CTAB +additives). As mentioned in the modeling section, Eqs. (18)-(20) belong to the aqueous mixtures of CTAB and additives. The parameters listed in Table 2 were used for these equations. Eq. (16) was applied to the calculation  $\omega_0$ . As an example, Figs. 3 and 4 show the experimental and computed surface tensions. The calculation results have been given in Table 3. The  $AAD$  was 5.05 for the applied mixed solutions.

Also, the present model can simultaneously predict the surface pressure ( $\pi$ ) or surface tension ( $\gamma$ ) and the surface coverage ( $\theta$ ) for (CTAB +additive) solutions. For instance, the surface coverage in terms of CTAB concentration has been plotted in Figs. 5 and 6. The obtained results prove that the surface coverage of CTAB decreases when it is applied in the presence of additives.

**Table 3: Experimental and computed surface tensions for the aqueous solutions of CTAB in presence of different concentrations of additives at  $T = 298.15$  K and  $P = 1$ atm.**

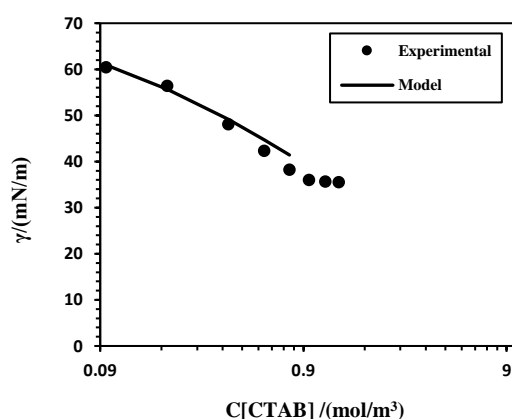
C/(mol/m <sup>3</sup> )	$\gamma_{\text{exp}}$ /(mN/m)	$\gamma_{\text{cal}}$ /(mN/m)	C/(mol/m <sup>3</sup> )	$\gamma_{\text{exp}}$ /(mN/m)	$\gamma_{\text{cal}}$ /(mN/m)	C/(mol/m <sup>3</sup> )	$\gamma_{\text{exp}}$ /(mN/m)	$\gamma_{\text{cal}}$ /(mN/m)
(90%CTAB+10%Acetonitrile)			(60%CTAB+40%Acetonitrile)			0.878	35.92	-
0.123	60.26	59.20	0.082	60.91	61.92	1.097	35.84	-
0.247	53.62	53.45	0.164	55.98	56.97	1.317	36.20	-
0.494	43.06	46.45	0.329	48.97	50.68	(70%CTAB+30%Tetrahydrofuran)		
0.741	36.31	-	0.494	43.73	46.45	0.096	61.98	60.60
0.987	35.64	-	0.658	39.29	43.22	0.192	54.55	55.20
1.234	35.55	-	0.823	37.35	40.60	0.384	47.59	48.53
1.481	35.11	-	0.988	35.09	-	0.576	41.41	44.13
(80%CTAB+20%Acetonitrile)			1.152	34.86	-	0.768	36.85	40.81
0.109	62.32	60.04	(90%CTAB+10%Tetrahydrofuran)			0.816	35.58	-
0.219	53.32	54.52	0.123	58.89	58.80	0.864	35.93	-
0.439	45.56	47.72	0.247	50.52	52.92	0.912	35.39	-
0.658	39.41	43.22	0.494	41.87	45.84	0.960	36.16	-
0.878	35.27	-	0.741	37.50	41.24	1.152	35.86	-
1.097	35.15	-	0.802	35.79	-	(60%CTAB+40%Tetrahydrofuran)		
1.317	35.04	-	0.988	35.48	-	0.082	61.25	61.62
1.536	35.05	-	1.235	35.15	-	0.164	52.69	56.52
(70%CTAB+30%Acetonitrile)			1.481	34.95	-	0.329	47.84	50.12
0.096	60.38	60.95	(80%CTAB+20%Tetrahydrofuran)			0.494	42.43	45.84
0.192	56.39	55.68	0.109	59.91	59.67	0.658	39.82	42.61
0.384	48.07	49.12	0.219	54.45	54.01	0.823	36.60	39.99
0.576	42.29	44.74	0.439	45.32	47.12	0.864	35.59	-
0.768	38.20	41.42	0.658	38.87	42.61	0.988	35.48	-
0.960	35.99	-	0.713	38.12	41.68	1.152	35.15	-
1.152	35.64	-	0.768	36.75	-	1.317	35.10	-
1.344	35.46	-	0.823	36.47	-			

**Table 4: Variation of CMC (mol/m<sup>3</sup>) value for CTAB solution in presence of different additives at the temperature of 298.15 K and  $P = 1$ atm by measuring surface tension.**

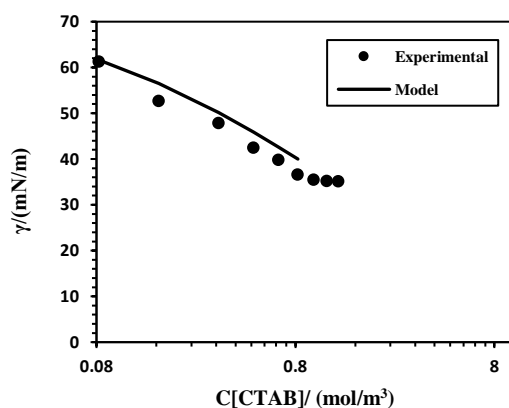
Weight percent (wt%) of additives	CTAB	CTAB + Acetonitrile	CTAB +Tetrahydrofuran
0	0.823	0.823	0.823
10	-	0.864	0.802
20	-	0.878	0.878
30	-	0.960	0.864
40	-	0.988	0.987

**Table 5: Variation of CMC (mol/m<sup>3</sup>) value for CTAB solution in presence of different additives at the temperature of 298.15 K and P=1atm by measuring conductivity.**

Weight percent (wt%) of additives	CTAB	CTAB + Acetonitrile	CTAB +Tetrahydrofuran
0	0.811	0.823	0.823
10	-	0.885	0.834
20	-	0.918	0.856
30	-	0.940	0.880
40	-	0.965	1.011

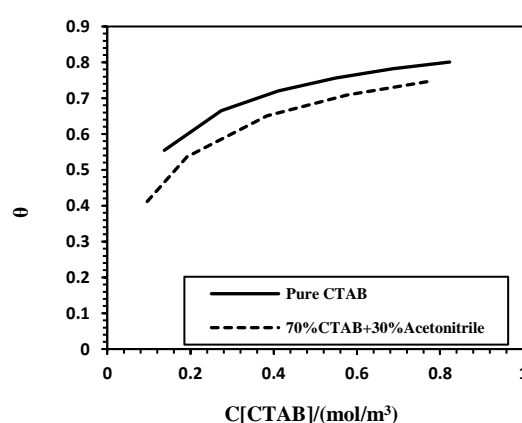


**Fig. 3: Experimental and predicted surface tensions of CTAB solution ( $\gamma$ ) in terms of CTAB concentration at  $T = 298.15$  K in presence of 30 wt% acetonitrile.**

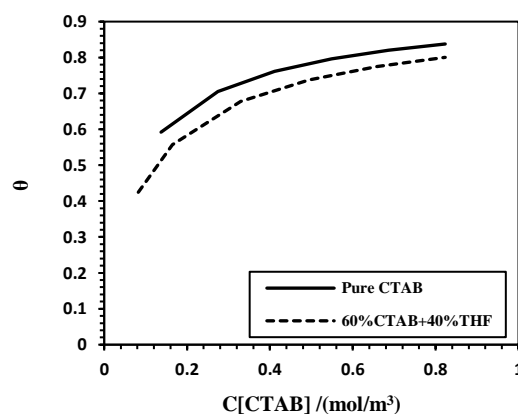


**Fig. 4: Experimental and predicted surface tensions of CTAB solution ( $\gamma$ ) in terms of CTAB concentration at  $T = 298.15$  K in presence of 40 wt% tetrahydrofuran.**

The addition of an additive to an aqueous solution of a surfactant results in increasing the hydrophobicity of the liquid phase. Hence, more hydrophobic tails of CTAB can remain in the liquid phase. Such an effect can decrease the absorption of the molecules of CTAB in the surface



**Fig. 5: Surface coverage ( $\theta$ ) versus CTAB concentration for the aqueous solution of pure CTAB and aqueous solution of CTAB in the presence of 30 wt% acetonitrile at  $T = 298.15$  K.**



**Fig. 6: Surface coverage ( $\theta$ ) versus CTAB concentration for the aqueous solution of pure CTAB and an aqueous solution of CTAB in the presence of 40 wt% tetrahydrofuran at  $T = 298.15$  K.**

layer, so the surface coverage of CTAB in the presence of additives is less than the one without the presence of additives. The present model was successful to describe the effect of additives on the interfacial behavior of the aqueous solutions.



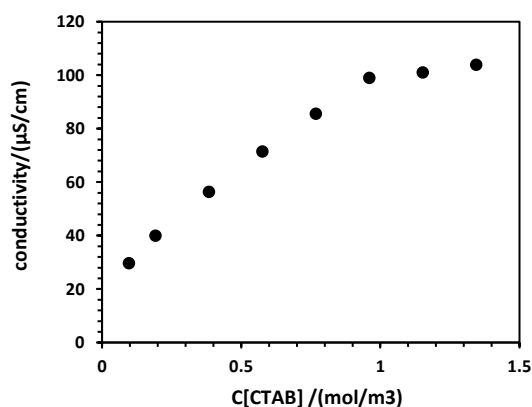


Fig. 7: Conductivity of CTAB solution in terms of CTAB concentration at  $T = 298.15$  K in presence of 30 wt% acetonitrile.

In the present study, the conductivity of aqueous solutions of CTAB and CTAB+acetonitrile and tetrahydrofuran were measured at various concentrations. It is known that the conductivity of the ionic surfactant increases as the concentration of the surfactant increases. At the critical micelle concentration and higher concentrations, the molecules of surfactants aggregate and form the micellar macroion, so they have lower mobility. As a result, the slope of conductivity in terms of surfactant concentration changes detectably. This point shows the CMC for a given surfactant. For instance, the conductivity of (CTAB+additives) has been shown in Figs. 7 and 8. These obtained CMCs are in good agreement with the ones obtained based on the surface tension measurements.

## CONCLUSIONS

The present was dedicated to studying the aqueous solutions of CTAB, acetonitrile, and tetrahydrofuran. Firstly, the measurements of the surface tensions were conducted for these solutions at  $T=298.15$  K, the ambient pressure, and various concentrations. A theoretical thermodynamic model was used to describe the behavior of the surface layer. The parameters of this model were fitted by using experimental data. The results proved that the thermodynamic model was able to reproduce changes in surface tension with concentration. The next measurements of the surface tensions were conducted for the aqueous solutions of (CTAB +additives). Subsequently, the CMC of the mixed aqueous solutions were measured based on the surface tension and conductivity. According to the results, the presence of additives led to increasing the values of CMC.

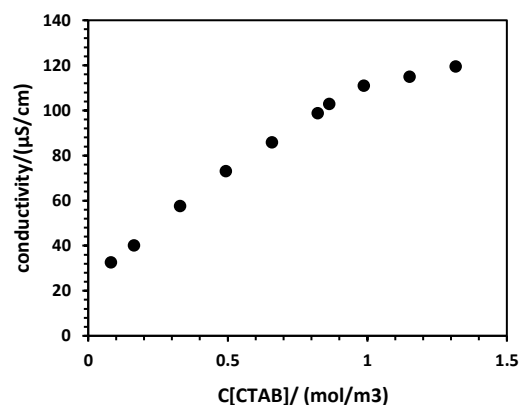


Fig. 8: Conductivity of CTAB solution in terms of CTAB concentration at  $T = 298.15$  K in presence of 40 wt% tetrahydrofuran.

Moreover, the model successfully predicted the surface tension of (CTAB+ additives) ( $AAD\% = 5.054$ ). Based on the computed surface coverage ( $\theta$ ) of CTAB, it can be concluded that the presence of additives can reduce the surface coverage of CTAB.

## Nomenclature

A	Interaction parameter
b	Surface-to-solution distribution constant
c	Concentration
$d_e$	Maximum diameter of the droplet, m
$d_s$	Small droplet diameter, m
f	Activity coefficient
g	Gravitational constant
H	Shape factor of a droplet
N	Number of experimental data
R	Ideal gas constant
T	Temperature
V	Molar volume
x	Mole fraction

## Abbreviations

AAD	Average absolute deviation
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## Greek letters

A	Bulk phase
$\Gamma$	Surface tension
$\Gamma$	Surface excess
$\Theta$	Surface coverage
$\mu_i$	The chemical potential of component i

$\pi$	Surface pressure
$\rho$	Density
$\Delta$	Difference
$\omega$	Molar area

**Subscripts**

B	Bulk
c	Critical
calc	Calculation
exp	Experimental
I	Component i
S	Surface
0	Water
1	Surfactant or additive

Received : Jul. 17, 2020 ; Accepted : Nov. 16, 2020

**REFERENCES**

- [1] Wang G., Yin Q., Shen J., Bai Y., Ma X., Du Z., Wang W., Surface Activities and Aggregation Behaviors of Cationic - Anionic Fluorocarbon - Hydrocarbon Surfactants in Dilute Solutions, *J. Mol. Liq.*, **234**: 142-148 (2017).
- [2] Banjare M.K., Kurrey R., Yadav T., Sinha S., Satnami M.L., Ghosh K.K., A Comparative Study on the Effect of Imidazolium-Based Ionic Liquid on Self-Aggregation of Cationic, Anionic and Nonionic Surfactants Studied by Surface Tension, Conductivity, Fluorescence and FTIR Spectroscopy, *J. Mol. Liq.*, **241**: 622-632 (2017).
- [3] Shah S.K., Chatterjee S.K., Bhattarai A., Micellization of Cationic Surfactants in Alcohol-Water Mixed Solvent Media, *J. Mol. Liq.*, **222**: 906-914 (2016).
- [4] Sadeghi R., Solaimani S., Ebrahimi N., Thermodynamic Properties of Anionic Surfactant/Polymer/Water Systems with Respect to Polymer-Surfactant Interactions and Salting Effect of Surfactant on Polymer in Aqueous Solutions, *Fluid Phase Equilib.*, **425**: 411-420 (2016).
- [5] Bhattacharya M., Dixit S., Study of Mixed Micelles of Sodium Dodecyl Sulphate and Nonionic Surfactants Polysorbates Tween Series: Their Interaction and Thermodynamic Parameter Using Cyclic Voltammetry, *Int. J. Chem. Stud.*, **3**: 22-25 (2015).
- [6] Esmaeili H., Esmaeilzadeh F., Mowla D., Effect of Surfactant on Stability and Size Distribution of Gas Condensate Droplets in Water, *J. Chem. Eng. Data.*, **59(5)**: 1461-1467 (2014).
- [7] Esmaeili H., Esmaeilzadeh F., Mowla D., Effect of Salinity, pH, and Temperature on Stability of Gas Condensate in Water Emulsions Using Different Surfactants, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **38(3)**: 151-166 (2019).
- [8] Tamjidi S., Esmaeili H., Chemically Modified CaO/Fe<sub>3</sub>O<sub>4</sub> Nanocomposite by Sodium Dodecyl Sulfate for Cr (III) Removal from Water, *Chem. Eng. Tech.*, **42(3)**: 607-616 (2019).
- [9] Homendra N., Devi CH.I., Micellar Behavior of Mixed Surfactant System of Linear Alkyl Benzene Sulfonate and Triton X-100 in Pure and Hard Water, *J. Surface Sci. Technol.*, **22**: 119-131 (2006).
- [10] K. Manna, Panda A.K., Physicochemical Studies on the Interfacial and Micellization Behavior of CTAB in Aqueous Polyethylene Glycol Media, *J. Surfact. Deterg.*, **14**: 563-576 (2011).
- [11] Lee B.H., Effects of Various Alcohols and Salts on the Mixed Micellization of Cationic Surfactant (CPC) with Nonionic Surfactant (TX-100), *Colloid Interface Sci. Commun.*, **19**: 1-4 (2017).
- [12] Andreas J.M., Hauser E.A., Tucker W.B., Boundary Tension by Pendant Drops, *J. Phys. Chem.*, **42**: 1001-1019 (1938).
- [13] Misak M.D., Equations for Determining 1/H Versus S Values in Computer Calculations of Interfacial Tension by the Pendant Drop Method, *J. Colloid Interface Sci.*, **27**: 141-142 (1968).
- [14] Fainerman V.B., Miller R., Chemical Potentials and Equation of State of Surface Layers for a Model Assuming Two-Dimensional Compressibility of Adsorbed Molecules, *Colloid. Surface.*, **319**: 8-12 (2008).
- [15] Fainerman V.B., Miller R., Aksenenko E.V., Simple Model for Prediction of Surface Tension of Mixed Surfactant Solutions, *Adv. Colloid Interface Sci.*, **96**: 339-359 (2002).
- [16] Rafati A.A., Ghasemian E., Experimental and Theoretical Study of Surface Tension of Binary Mixtures of (n-alkyl Acetates + Heptane, Benzene, and Toluene), *J. Chem. Thermodyn.*, **41**: 386-391 (2009).

- [17] Poling B.E., Prausnitz J.M., O'Connell J.P., "The Properties of Gases and Liquids", 5th ed., McGraw-Hill, New York, (2000).
- [18] Mousavi N.S., Khosharay S., Investigation on the Interfacial Behavior of Aqueous Solutions of Cetyltrimethyl Ammonium Bromide in the Presence of Polyethylene Glycols, *Fluid Phase Equilib.*, **465**: 58-64 (2018).
- [19] Khosharay S., Talebi M., Akbari-Saeed T., Salehi-Talaghani S., Experimental and Modeling Study of the Surface Tension and Interface of Aqueous Solutions of Alcohols, Cetyltrimethylammonium Bromide (CTAB) and Their Mixtures, *J. Mol. Liq.*, **249**: 245–253 (2018).
- [20] Nist Chemistry Webbook Available from: <http://www.webbook.nist.gov/chemistry/fluid/>.
- [21] Wei L., Ming Z., Jinli Z., Yongcai H., Self-Assembly of Cetyltrimethylammonium Bromide in Ethanol-Water Mixtures, *Front. Chem. China*, **4**: 438-442 (2006).