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Experimental and modeling study of the surface tension and interface of aqueous solutions of alcohols, cetyltrimethylammonium bromide (CTAB) and their mixtures

Shahin Khosharay *, Mehrnoosh Talebi, Tala Akbari Saeed, Sepideh Salehi Talaghani

Iranian Institute of Research & Development in Chemical Industries (IRDCI-ACECR), Tehran, Iran

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ABSTRACT

In this study, the experimental surface tensions were measured for aqueous solutions of cetyltrimethyl ammonium bromide, 1-propanol, 2-propanol, and 1-butanol with a pendant drop apparatus. The temperature and pressure of all experiments were 298.15 K and 1 bar, respectively. Subsequently, a model based on the equality of the chemical potential of components at the interface and the bulk liquid was used. The results of this part showed that the surface tensions were reproduced well. The average absolute deviation percent of surface tension was 1.11. Then the surface tensions of (cetyltrimethylammonium bromide + alcohols) aqueous mixtures were measured at different concentrations. Moreover, the critical micelle concentrations of the applied systems were determined. The present model was used for aqueous mixtures of (cetyltrimethylammonium bromide + alcohols). The average absolute deviation percent of surface tension was 2.72, so the model successfully predicted the surface tension for aqueous solutions of (cetyltrimethylammonium bromide + alcohols). Furthermore, the results of the model proved that the presence of alcohols decreased the surface coverage of cetyltrimethylammonium bromide and increased the values of the critical micelle concentration.

1. Introduction

Surfactant or surface active agent is a special group of chemical substances made up of a hydrophilic head and a hydrophobic tail. Since surfactants adhere to the interface, they can decrease the surface tension. The reduction in surface tension is a fundamental property of surfactants. This property leads to the widespread application of surfactants in commodity chemicals, agrochemicals, detergents, foam, oil exploration, food processing, and emulsion stabilizers [1–3].

A single surfactant is not usually enough to provide all required properties in many cases, so it is used in the presence of appropriate additives. The presence of additives can strongly affect physicochemical properties of solution and interface. In order to compute the adsorption behavior of the mixed surface layers, the experimental surface tensions should be matched with a theoretical model. Many of these models need known characteristics of the individual components. Therefore, the equations of state used for mixed interfaces involve the isotherm parameters of pure components [4–6].

The influence of additives on the properties of surfactant solutions has been a subject of researches in recent years. Lee [7] measured the critical micelle concentrations of cetylpyridinium chloride (CPC) in the presence of polyoxyethylene (10) *p*-isooctylphenyl ether (TX-100). He computed different thermodynamic parameters for these solutions. The results showed that strong interactions exist between two surfactants in a micellar state. Shah et al. [8] studied the effect of methanol and ethanol on the micellization behavior of dodecyltrimethylammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB). They measured surface tension and conductivity of aqueous solutions at 298.15 K. Then they calculated various physicochemical properties. They concluded that alcohols can strongly affect the properties of DTAB and CTAB. Manna and Panda [9] studied the micellization and interface of cetyltrimethylammonium bromide (CTAB), PEG family and (CTAB + PEG family) by measuring the equilibrium surface tension at different concentrations. They found that PEG can increase the critical micelle concentration (CMC) of CTAB. Tomi et al. [10] used conductivity measurements, and they determined the micelle formation conditions of DTAB in the presence of alkanediols. The results of the experiments proved that alkanediols can increase the values of CMC. Mulqueen and Blankschtein [11] computed all parameters of the model for a mixture of (ionic + non-ionic) surfactants. They calculated the areas per molecule by using Monte Carlo simulations. Fainerman et al. [12] proposed a rigorous theoretical model to describe the interface of surfactant mixtures. This method could determine the molar areas and non-ideality of these systems. Zhi-guo and Hong [13] measured the surface tension of AEO9/sodium dodecyl sulfate (SDS) and AEO9/cetyltrimethylammonium bromide

* Corresponding author.
E-mail address: khosharay@irdci.ac.ir (S. Khosharay).

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(CTAB) mixtures. They determined critical micelle concentration (CMC), the maximum value of surface excess (Γ_{max}), and the minimum area per molecule at the air/liquid interface (A_{min}). Rezic [14] used Design Expert software to predict the lowest surface tension. They optimized the composition of various surfactant mixtures. The predictions were in a good agreement with experimental data. Zhang and Lam [15] reported the experimental surface tensions of the mixtures made up of nonionic and cationic surfactants. They determined the interactions between these surfactants.

In the present study, the surface tension has been measured for aqueous solutions of CTAB, 1-propanol, 2-propanol, and 1-butanol at the temperature of 298.15 K. The pendant drop technique has been used for these measurements. The critical micelle concentration (CMC) is determined for CTAB. By using the equality of chemical potentials of components at the interface and bulk liquid, the molar area, surface-to-solution distribution constant, and interactions have been regressed for CTAB and each alcohol. Then the surface tension of (CTAB + 1-propanol), (CTAB + 2-propanol), and (CTAB + 1-butanol) aqueous mixtures are measured at different concentrations. According to the surface tension measurements, the CMC of these mixed systems has been determined. Moreover, by using the obtained parameters of the pure CTAB and alcohols, the surface tension of solutions and surface coverage of surfactants is predicted for these aqueous mixtures, and the interfacial behavior of each mixture has been discussed.

2. Experimental

2.1. Material used

The cationic surfactant, CTAB (cetyl trimethyl ammonium bromide), was supplied by Merck, Germany. It had a purity of 97%. Alcohols, including methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol with a purity of 99% were purchased from Merck, Germany. To our knowledge, methanol and ethanol were only used to test the validity of experimental surface tensions. Also, distilled water was used during each experiment. In order to prepare aqueous solutions, an electronic balance with an uncertainty of 0.1 mg was utilized to weight CTAB and alcohols. The details of the materials are in Table 1.

2.2. Apparatus

The schematic of the experimental apparatus has been shown in Fig. 1. All experiments were carried out in a cylindrical Pyrex cell. The capacity of the cell was 500 cm^3. The cell was also equipped with two sight glasses, which allowed a user to observe the droplet shape from the horizontal axis. This cell could operate at atmospheric pressure and the temperature range of 275.15 K to 373.15 K. The temperature was measured using a thermometer with an uncertainty of ±0.1 K. The cell had a jacket through which a fluid could flow and control the cell temperature. It had a glass capillary tube for hanging a droplet. The inner and outer diameters of this capillary tube are 1.2 mm and 1.587 mm, respectively. A glass needle valve was used to inject the liquid sample into the cylinder chamber and form a pendant drop. This system was also equipped with a digital camera and a light source that helps a researcher capture the droplet images and measure the surface tension. This digital camera was connected to a personal computer.

Table 1
The applied materials in this study.

Chemical	Purity	Supplier
CTAB	97%	Merck, Germany
Methanol	99%	Merck, Germany
Ethanol	99%	Merck, Germany
1-Propanol	99%	Merck, Germany
2-Propanol	99%	Merck, Germany
1-Butanol	99%	Merck, Germany

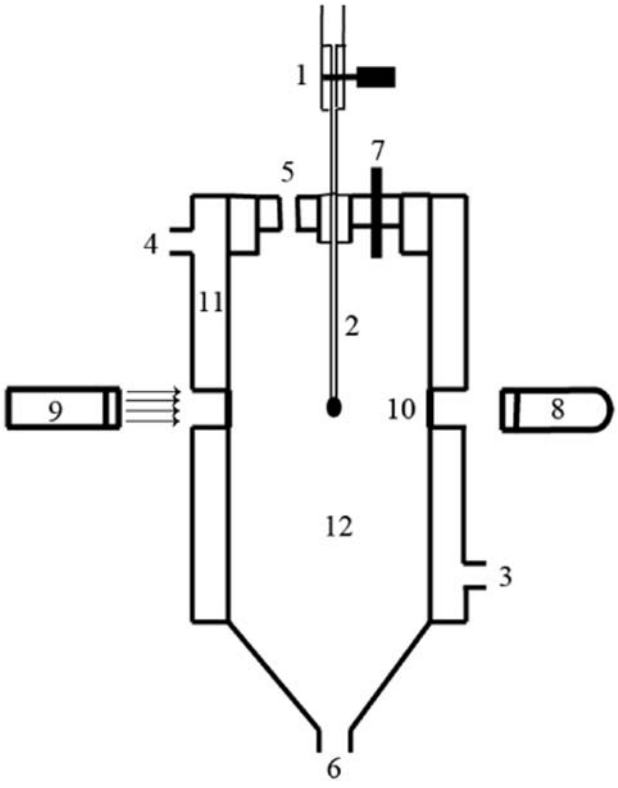

Fig. 1. The schematic of the apparatus for measuring the surface tension of surfactant solutions (pendant drop), 1. Needle valve; 2. Glass capillary tube; 3. Inlet of the jacket; 4. Outlet of the jacket; 5. Inlet of the air; 6. To the vacuum; 7. Thermometer; 8. Digital Camera; 9. Light source; 10. Sight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

2.3. The experimental procedure

Prior to any experiments, the capillary tube and needle valve were rinsed for three times with distilled water by using the following procedure. The vacuum pump was turned on. This resulted in the suction and air flow through the cell. Then the air inlet was closed, and a proper amount of distilled water was injected through the needle valve and capillary tube. The suction led to a flow of the distilled water into the needle valve tube and the capillary tube, so they were washed. After the washing process was finished, the air inlet was opened. The air was allowed to flow through the cell, capillary tube, and needle valve for 10 min. This flow of the air was necessary to dry the cell, capillary tube, and needle valve. Subsequently, the specified aqueous solution was introduced slowly into the cell through the needle valve and a glass capillary tube. This aqueous solution formed a pendant drop at the tip of the glass capillary tube, and it was vertically inserted into the cell. The images of the droplet were captured with the digital camera, and the surface tension of each aqueous solution was measured. In this study, the surface tension was measured by using the equations proposed by Andreas et al. [16].

$$\gamma = \frac{\Delta\rho d_e^2 g}{H} \tag{1}$$

$$\frac{1}{H} = f\left(\frac{d_s}{d_e}\right) \tag{2}$$

In Eqs. (1) and (2), $\Delta\rho$shows the density difference between the liquid phase and the air, g is the gravitational constant, d_s corresponds to the droplet diameter at the height which is equal to the maximum diameter of the droplet (d_e). The relation between $\frac{1}{H}$ and $\frac{d_s}{d_e}$ was taken

from the study of Drelich et al. [17]. A glass pycnometer with a volume of 25 cm^3 was used to measure the density of the liquid phase.

3. Model description

In the present study, the equality of chemical potentials in the liquid phase and interface is considered to model the interface of the aqueous surfactant solutions. The detailed description of this model is in [12, 18–20]; therefore, the significant equations are explained here.

When the partial molar surface area is independent of surface tension, the chemical potential of the components can be expressed as follows:

$$\mu_i^S = \mu_i^{0S} + RT\ \ln\left(f_i^S x_i^S\right) - \gamma\omega_i \tag{3}$$

In Eq. (3), μ_i is the chemical potential of each component in the aqueous solution, γshows the surface tension of an aqueous surfactant solution, f indicates the activity coefficient, and ω belongs to the partial molar surface area. x_i is the mole fraction of each component in the aqueous solution. Superscripts S and 0 relate to the interface and the standard state, respectively. Also, the chemical potential of the components in the bulk aqueous solution can be expressed as follows:

$$\mu_i^\alpha = \mu_i^{0\alpha} + RT\ \ln\left(f_i^\alpha x_i^\alpha\right) \tag{4}$$

In Eq. (4), α denotes the bulk phase.

Based on the thermodynamic equilibrium, the chemical potentials of components have to be equal in the bulk solution and interface. Therefore, the right sides of Eqs. (3) and (4) for solvent and solute are equal. Considering standard state for the solvent ($i = 0$), $x_0^\alpha = x_0^S = 1$, and $f_0^\alpha = f_0^S = 1$. The standard state of the solute ($i = 1$) is the infinite dilution, including$x_1^\alpha \to 0, f_1^\alpha = f_1^S = 1$, and $\gamma = \gamma_0$ (γ_0 shows the surface tension of a pure solvent). When the above assumptions are used, the following equations are obtained:

$$\Pi = -\frac{RT}{\omega_0}\left(\ \ln x_0^S + \ \ln f_0^S\right) \tag{5}$$

$$\ln\frac{f_1^S x_1^S / f_{10}^S}{K_1 f_1^\alpha x_1^\alpha} = \frac{\omega_1}{\omega_0}\left(\ \ln x_0^S + \ \ln f_0^S\right) \tag{6}$$

Table 2
The comparison between the measured values of surface tension (mN/m) in the present study and the results of other studies in literature at the temperature of 298.15 K [19–30].

Chemical	γ (mN/m) (present study)	γ (mN/m) (literature)
Water	71.70	72.01 [19]
		72.01 [20]
		72.09 [21]
		72.08 [22]
Methanol	23.18	22.51 [19]
		22.64 [23]
Ethanol	22.62	21.82 [19]
		21.95 [23]
1-Propanol	23.38	23.28 [19]
		22.50 [24]
		22.98 [25]
		23.32 [23]
2-Propanol	21.00	21.22 [19]
		20.90 [26]
		20.95 [27]
		21.05 [23]
1-Butanol	23.56	23.79 [28]
		23.70 [29]
		23.47 [30]

Table 3
The experimental and calculated surface tensions for the aqueous solutions of pure CTAB, 1-propanol, 2-propanol, and 1-butanol at the temperature of 298.15 K and different concentrations.

C(mmol/lit)	γ_{exp}(mN/m)	γ_{calc}(mN/m)		
		Frumkin's model	Original model + Eq. (22)	Original model + Eq. (23)
CTAB				
0.137	49.07	50.42	53.59	51.85
0.274	47.66	44.35	46.91	47.65
0.411	44.99	40.78	42.40	42.80
0.548	38.25	38.25	38.93	39.10
0.685	36.11	36.28	36.10	36.11
0.823	33.56	–	–	–
0.850	33.47	–	–	–
0.878	33.5	–	–	–
1-Propanol				
8.32	67.08	68.47	67.60	68.49
16.64	67.07	67.60	67.02	67.61
24.96	67.02	67.02	66.57	67.02
33.28	66.66	66.57	66.20	66.56
41.60	66.28	66.20	65.89	66.18
49.92	65.89	65.89	65.37	65.86
66.56	64.88	65.37	64.94	65.33
83.20	63.71	64.94	67.60	64.89
2-Propanol				
1.663	68.88	69.00	70.01	70.01
3.327	68.77	68.64	69.42	69.42
4.991	68.77	68.33	68.99	68.99
6.655	68.64	67.70	68.63	68.63
8.319	68.30	67.20	68.33	68.32
12.47	67.71	66.43	67.71	67.71
16.63	66.89	65.82	67.21	67.21
24.95	66.15	65.33	66.44	66.44
33.27	65.64	64.90	65.84	65.84
41.59	65.11	67.70	65.34	65.34
49.91	64.91	67.20	64.91	64.91
66.55	64.20	64.20	64.19	64.19
83.19	63.67	63.62	63.59	63.59
1-Butanol				
4.047	67.75	68.65	68.59	68.22
5.396	67.77	68.16	68.13	67.77
6.745	67.74	67.74	67.74	67.38
10.11	67.6	66.89	66.93	66.61
13.49	67.15	66.21	66.28	66.00
26.98	64.64	64.38	64.45	64.32
40.47	63.20	63.20	63.19	63.20
53.96	61.08	62.32	62.22	62.33
67.45	58.58	61.61	61.41	61.63

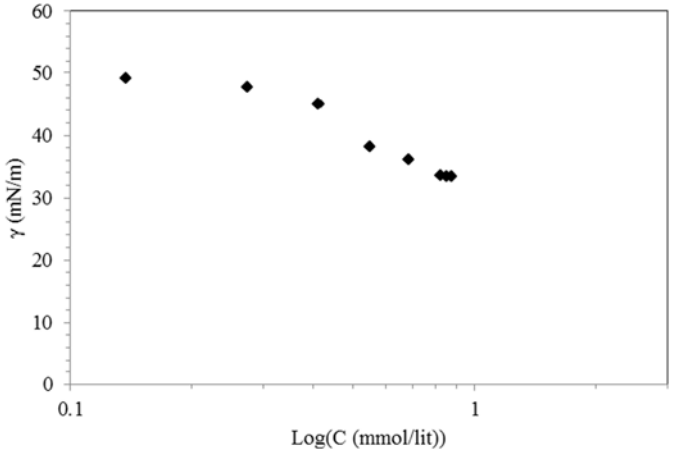

Fig. 2. The changes of the surface tension with the logarithm of the total concentration for the aqueous solution of CTAB at the temperature of 298.15 K.

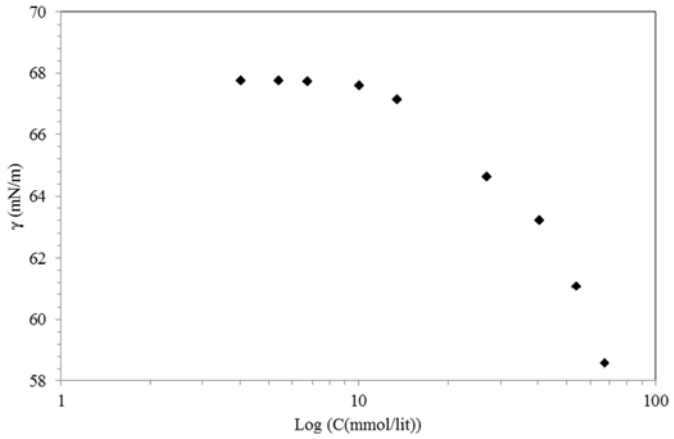

Fig. 3. The changes of the surface tension with the logarithm of the total concentration for the aqueous solution of 1-butanol at the temperature of 298.15 K.

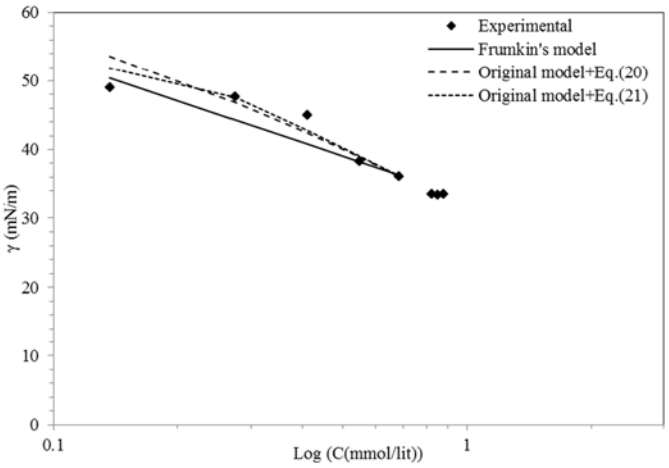

Fig. 4. Performances of different models for the aqueous solution of CTAB at the temperature of 298.15 K.

In this model, the distribution constant at infinite dilution of solute is $K_1 = (x_1^S/x_1^\alpha)_{\Pi=0}$, f_{10}^S is considered for such dilution. Also, $\Pi = \gamma_0\text{-}\gamma$ shows the surface pressure.

The general relation between the interfacial mole fraction (x_k^S) and surface coverage (θ_k) is defined as follows:

$$x_k^S = \frac{\theta_k}{n_k \sum_{i\geq 0}(\theta_i/n_i)} \quad n_i = \omega_i/\omega_0 \tag{7}$$

In Eq. (7), ω_0 and ω_i are the molar area of solvent and surfactants, respectively. In the above equation, $\theta_k = \Gamma_k\omega_k$.

The equations of the activity coefficients in the interface are computed as follows:

$$\ln f_0^S = \ln\left(1-\left(1-\frac{1}{n_1}\right)\theta_1\right) + \left(1-\frac{1}{n_1}\right)\theta_1 + a\theta_1^2 \tag{8}$$

$$\ln f_1^S = \ln(n_1 + (1-n_1)\theta_1) + (1-n_1)(1-\theta_1) + an_1\theta_0^2 \tag{9}$$

$$\ln f_{10}^S = \ln n_1 + (1-n_1) + an_1 \tag{10}$$

Introducing Eqs. (8)–(10) into Eqs. (5) and (6) and considering $f_1^\alpha = 1$, the following equation of state (original model) is obtained for the interface:

$$\Pi = -\frac{RT}{\omega_0}\left(\ln(1-\theta_1) + \left(1-\frac{1}{n_1}\right)\theta_1 + a{\theta_1}^2\right) \tag{11}$$

$$bc = \frac{\theta_1}{n_1(1-\theta_1)^{n_1}}\exp(-2an_1\theta_1) \tag{12}$$

When ω_1 is set equal to ω_0, Eqs. (11) and (12) are expressed as follows:

$$\Pi = -\frac{RT}{\omega}\left(\ln(1-\theta_1) + a{\theta_1}^2\right) \tag{13}$$

$$bc = \frac{\theta_1}{1-\theta_1}\exp(-2a\theta_1) \tag{14}$$

This model is known as Frumkin's model [12,18–20].

For a mixture of two surfactants or (additive + surfactant), the (original) model is expressed as follows:

$$\Pi = -\frac{RT}{\omega_0}\Big(\ln(1-\theta_1-\theta_2) + \theta_1\left(1-\frac{1}{n_1}\right) + \theta_2\left(1-\frac{1}{n_2}\right) + a_1{\theta_1}^2 + a_2{\theta_2}^2 + 2a_{12}\theta_1\theta_2\Big) \tag{15}$$

$$b_ic_i = \frac{\theta_i}{(1-\theta_1-\theta_2)^{n_i}}\exp(-2a_i\theta_i - 2a_{12}\theta_j)\exp\Big((1-n_i)\left(a_1\theta_1^2 + a_2\theta_2^2 + 2a_{12}\theta_1\theta_2\right)\Big) \tag{16}$$

For a mixture of two surfactants or (additive + surfactant), Frumkin's model is stated as follows:

$$\Pi = -\frac{RT}{\omega}\Big(\ln(1-\theta_1-\theta_2) + a_1{\theta_1}^2 + a_2{\theta_2}^2 + 2a_{12}\theta_1\theta_2\Big) \tag{17}$$

$$b_ic_i = \frac{\theta_i}{1-\theta_1-\theta_2}\exp(-2a_i\theta_i - 2a_{12}\theta_j) \tag{18}$$

In Eqs. (15)–(18), a_{12} is computed as follows:

$$a_{12} = \frac{a_1 + a_2}{2} \tag{19}$$

In Eq. (17), ω is obtained as follows:

$$\omega = \frac{\Gamma_1\omega_1 + \Gamma_2\omega_2}{\Gamma_1 + \Gamma_2} \tag{20}$$

For an aqueous solution of a single surfactant, the required input of the model is temperature. When simplification of Frumkin's model is

Table 4
The molar area, surface-to-solution distribution constant, and interactions of aqueous solutions of pure CTAB, 1-Propanol, 2-Propanol, and 1-Butanol by using different models.

Chemical	Frumkin's model			Original model + Eq. (22)			Original model + Eq. (23)		
	$\omega \times 10^{-5}$ (m^2/mol)	b (lit/mmol)	*a*	$\omega \times 10^{-5}$ (m^2/mol)	b (lit/mmol)	*a*	$\omega \times 10^{-5}$ (m^2/mol)	b (lit/mmol)	*a*
CTAB	2.801	9.9348	2.004	1.099	10.272	−0.695	1.413	9.9394	−0.138
1-Propanol	3.822	0.2506	−6.509	1.503	0.0384	−6.456	2.789	0.05719	−2.597
2-Propanol	6.675	0.2495	−1.516	1.616	0.0237	−2.921	2.110	0.03885	−2.788
1-Butanol	7.097	0.2846	−0.362	1.571	0.0300	−1.908	1.998	0.07975	−2.862

Table 5
The experimental surface tensions of aqueous solutions of alcohol + CTAB and the computed surface tensions with the original model + Eq. (23) at the temperature of 298.15 K and different concentrations.

C(mmol/lit)	γ_{exp}(mN/m)	γ_{cal}(mN/m)
(10 wt%1-Propanol + 90 wt% CTAB)		
0.206	59.39	58.71
0.413	51.95	52.42
0.620	47.78	48.04
0.826	43.47	44.64
1.033	40.48	41.86
1.136	37.88	40.63
1.240	36.09	–
1.343	36.18	–
1.446	36.06	–
1.653	36.00	–
(20 wt%1-Propanol + 80 wt% CTAB)		
0.276	60.50	59.63
0.552	53.80	53.60
0.828	48.17	49.36
1.104	44.77	46.06
1.380	42.05	43.34
1.657	40.75	41.03
1.933	37.53	39.01
2.209	34.24	–
2.485	34.21	–
3.037	33.68	–
3.314	33.50	–
(30 wt%1-Propanol + 70 wt% CTAB)		
0.345	60.26	60.59
0.691	54.83	54.87
1.036	50.04	50.81
1.382	48.27	47.61
1.728	44.27	44.98
2.073	42.70	42.73
2.419	40.32	40.76
2.765	38.20	39.01
3.110	37.20	37.43
3.456	35.24	–
3.802	35.19	–
4.147	35.19	–
(40 wt%1-Propanol + 60 wt% CTAB)		
0.415	62.77	61.63
0.831	57.92	56.28
1.246	52.29	52.41
1.662	50.51	49.35
2.493	43.51	44.63
2.909	41.14	42.73
3.324	39.94	41.02
3.740	38.02	39.49
4.155	37.36	38.09
4.571	35.95	–
4.987	35.58	–
5.402	35.60	–
5.818	35.47	–
(10 wt%2-Propanol + 90 wt% CTAB)		
0.206	59.80	58.71
0.413	54.22	52.42
0.620	50.69	48.03
0.826	46.19	44.64
1.033	40.93	41.85
1.240	36.78	39.49
1.446	32.33	–
1.653	32.15	–
2.066	32.51	–
(20 wt%2-Propanol + 80 wt% CTAB)		
0.276	60.04	59.62
0.552	56.74	53.59
0.828	50.15	49.35
1.104	44.93	46.05
1.380	41.11	43.34
1.657	38.46	41.02
1.822	35.77	–
1.933	35.59	–
2.209	35.08	–
2.761	34.19	–
(30 wt%2-Propanol + 70 wt% CTAB)		
0.345	61.96	60.59
0.691	57.34	54.87
1.036	53.62	50.80
1.382	50.69	47.61
1.728	47.30	44.98
2.073	43.74	42.72
2.419	40.36	40.76
2.765	36.64	39.01
3.318	34.18	–
3.456	34.17	–
4.147	33.20	–
(40 wt%2-Propanol + 60 wt% CTAB)		
0.415	62.95	61.63
0.830	57.06	56.27
1.245	53.41	52.40
1.660	48.20	49.35
2.075	46.35	46.81
2.490	44.57	44.63
2.906	42.57	42.72
3.321	39.33	41.02
4.151	36.77	38.08
4.815	33.09	–
4.981	33.49	–
5.812	33.75	–
(10 wt%1-Butanol + 90 wt% CTAB)		
0.190	61.25	58.71
0.381	55.04	52.42
0.572	49.73	48.03
0.763	46.61	44.64
0.954	44.31	41.85
1.145	40.03	39.49
1.260	36.89	–
1.336	36.86	–
1.527	36.83	–
1.909	36.11	–
(20 wt%1-Butanol + 80 wt% CTAB)		
0.244	60.81	59.61
0.489	54.23	53.59
0.734	48.56	49.35
0.978	45.67	46.05
1.223	44.33	43.33
1.468	43.28	41.02
1.614	41.08	39.78
1.712	34.61	–
1.957	34.47	–
2.936	34.31	–
(30 wt%1-Butanol + 70 wt% CTAB)		
0.298	62.22	60.58
0.596	56.06	54.86
0.895	52.27	50.79
1.193	49.32	47.60
1.492	47.70	44.97
1.790	44.69	42.72
2.088	41.03	40.75
2.387	40.29	39.00
2.864	34.35	–
2.984	34.56	–
3.580	34.63	–
(40 wt%1-Butanol + 60 wt% CTAB)		
0.352	62.67	61.62
0.704	58.22	56.26
1.056	55.13	52.39
1.408	50.38	49.33
1.760	47.93	46.80
2.112	46.57	44.62
2.465	43.13	42.71
2.817	40.55	41.01
3.521	37.17	38.07
4.225	35.23	–
4.401	35.05	–
4.577	35.34	–

Table 6
The values of critical micelle concentration (CMC) for different systems at the temperature of 298.15 K.

System	CMC (mmol/lit)
CTAB	0.823
10 wt%1-Propanol + 90 wt% CTAB	1.240
20 wt%1-Propanol + 80 wt% CTAB	2.209
30 wt%1-Propanol + 70 wt% CTAB	3.456
40 wt%1-Propanol + 60 wt% CTAB	4.571
10 wt%2-Propanol + 90 wt% CTAB	1.446
20 wt%2-Propanol + 80 wt% CTAB	1.822
30 wt%2-Propanol + 70 wt% CTAB	3.318
40 wt%2-Propanol + 60 wt% CTAB	4.815
10 wt%1-Butanol + 90 wt% CTAB	1.260
20 wt%1-Butanol + 80 wt% CTAB	1.712
30 wt%1-Butanol + 70 wt% CTAB	2.864
40 wt%1-Butanol + 60 wt% CTAB	4.225

not used (Eqs. (11) and (12)), the molar area of the water is another input of the model. The surface coverage of the surfactant (θ_1) and surface pressure (Π) are unknowns of the model. These parameters, θ_1 and Π, are computed by simultaneous solution of Eqs. (11) and (12) or Eqs. (13) and (14) with Newton-Rophson method. a, b and ω are the adjustable parameters of the model obtained according to the minimization of average absolute deviation of surface tension (AAD_γ). AAD_γ is defined according to the following equation:

$$AAD_\gamma = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{\gamma_i^{exp}-\gamma_i^{calc}}{\gamma_i^{exp}}\right| \times 100 \qquad (21)$$

In Eq. (21), N is the number of experimental data. Subscripts exp. and calc shows experimental and calculation, respectively.

For an aqueous mixture of two surfactants or (additive + surfactant), the temperature and parameters of each pure surfactant (a_i, b_i and ω_i) are the required inputs of this model. When Eqs. (15) and (16) are applied, the molar area of the water is another input of the model. These parameters are the ones obtained based on the surface tension of each surfactant solution. Similar to the aqueous solution of the pure surfactant, the surface coverage of each surfactant (θ_i) and surface pressure (Π) are unknowns of the model. These unknowns are calculated by simultaneous solution of Eqs. (15) and (16) or Eqs. (17) and (18) with the Newton-Rophson method.

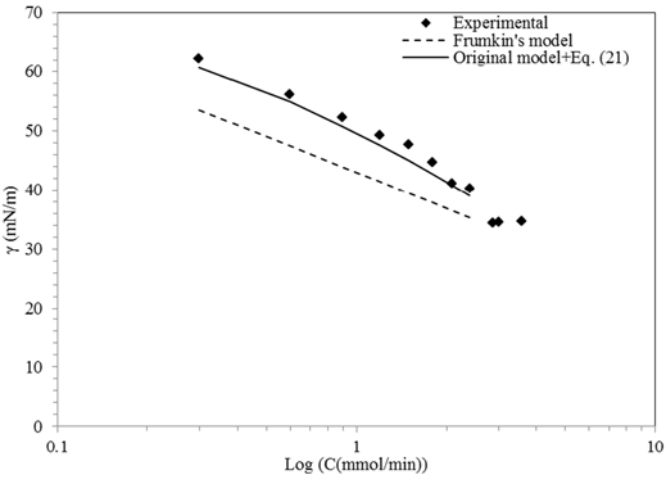

Fig. 5. The changes of the surface tension with the logarithm of the total concentration for the aqueous solution of (30 wt%1-Butanol + 70 wt% CTAB) at the temperature of 298.15 K.

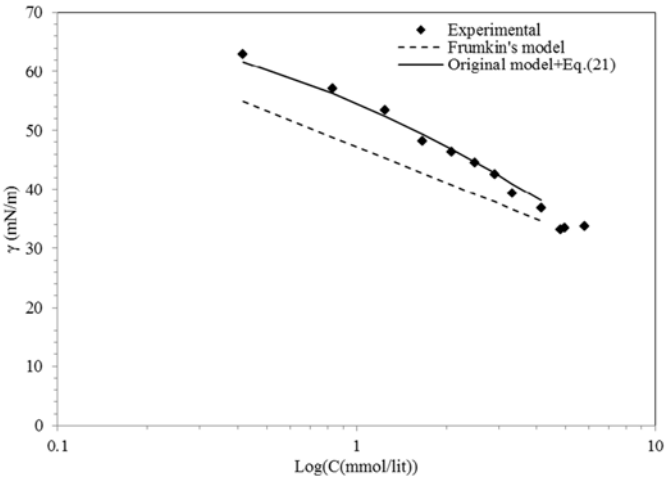

Fig. 6. The changes of the surface tension with the logarithm of the total concentration for the aqueous solution of (40 wt%2-propanol + 60 wt% CTAB) at the temperature of 298.15 K.

4. Results and discussion

Firstly, the surface tension was measured for aqueous solutions of CTAB, 1-propanol, 2-propanol, and 1-butanol. Each measurement was repeated for three times. All of these experiments were conducted at the temperature of 298.15 K. Since the validity of the measurement should be recognized, the surface tension of water, methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol was measured at 298.15 K and compared with the data reported in [19–30]. Table 2 proves that these measured surface tensions have good agreements with the ones in the literature.

The experimental surface tensions for the aqueous solutions of CTAB, 1-propanol, 2-propanol, and 1-butanol have been reported in Table 3. As an example, plots of surface tensions for the aqueous solutions of CTAB and 1-butanol have been presented in Figs. 2 and 3. When the concentration of CTAB increases in an aqueous solution, the surface tension of the system strongly decreases. The abrupt reduction of surface tension continues until it reaches a certain concentration. This concentration is the critical micelle concentration (CMC) of CTAB at which the decrease in the surface tension stops. According to the present measurements, the value of the CMC is 0.823 mmol/lit for CTAB. This value has been compared to the ones reported in the literature [9,31–33].

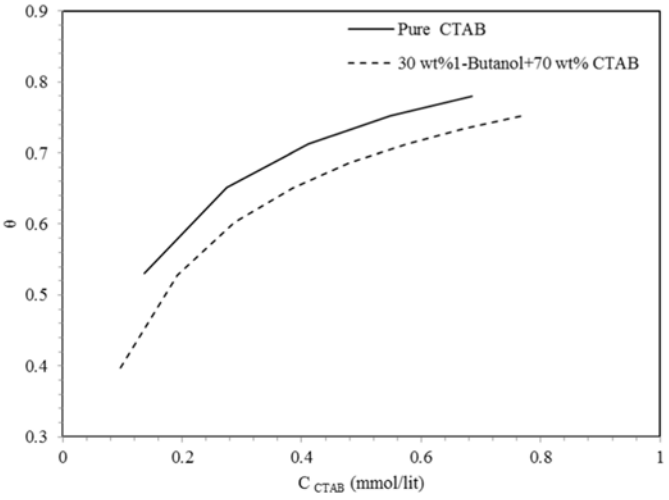

Fig. 7. The surface coverage of CTAB in terms of concentration of CTAB in the bulk liquid solution for the aqueous solution of pure CTAB and (30 wt%1-Butanol + 70 wt% CTAB).

The values of CMC were 0.8, 0.98, 0.8, 0.86 mmol/lit in [9,31–33]. The measured value of CMC is in a good agreement with the other values in literature. This comparison is another proof for the validity of apparatus and measurements.

The concentration dependence of surface tension values for alcohols is different from CTAB. This concentration dependence is relatively simple, and it has a steeper slope. This proves that alcohols have much weaker surface activity than CTAB. Also, the slope of the plot of surface tension against the concentration does not reach the value of zero slopes even at high concentrations. This result shows that it is impossible for molecules of alcohols to form micelles in water.

After the experimental measurements were done, the original model (Eqs. (11) and (12)) and the Frumkin's model [12,18,34] were used to determine the parameters of each pure CTAB and alcohols (a_i, b_i and ω_i). These parameters were regressed based on the experimental surface tension of aqueous solutions. To our knowledge, these models are applicable only for the concentrations which are lower than CMC. As mentioned in the previous section, Eqs. (11) and (12) require the molar area of the water as an input to the model. The present study used the following eqs [35,36]. for the molar area.

$$\omega_0 = N_a^{\frac{1}{3}} V_b^{\frac{2}{3}} \tag{22}$$

$$\omega_0 = 1.021 \times 10^8 V_c^{\frac{6}{15}} V_b^{\frac{4}{15}} \tag{23}$$

In Eqs. (22) and (23), V_b is the molar volume of the pure water at the specified temperature, and V_c is the critical molar volume of the water. The values of V_b and V_c are 18.069 $cm^3.mol^{-1}$ and 57.1 $cm^3.mol^{-1}$, respectively [37]. Firstly, the original model used Eq. (22) and then it applied Eq. (23) to describe the interface. The results of all models have been reported in Table 3 and Table 4. As an example, Fig. 4 compares the experimental surface tensions with the calculated ones for CTAB. Table 4 shows that alcohols have higher values of the partial molar surface area than CTAB. This shows that alcohols have a larger surface area per molecule. The other important parameter, the surface-to-solution distribution constant (b), is low for alcohols. Therefore, in comparison with CTAB, alcohols do not show high surface activity. Among the alcohols, the highest value of b is for 1-butanol. The original model in combination with Eq. (22) cannot reproduce changes of the surface tension with concentration for (water + 1-propanol) mixture. Moreover, based on the combination of the original model and Eq. (22), the highest value of b is for 1-propanol. It is not a logical result. Therefore, the selection of a suitable molar area of water plays a significant role in the original model. The original model used Eq. (23) and Frumkin's model is a suitable model for the aqueous solutions of pure CTAB and alcohols. The values of AAD_γ were 1.56 and 1.11 for these two models, respectively.

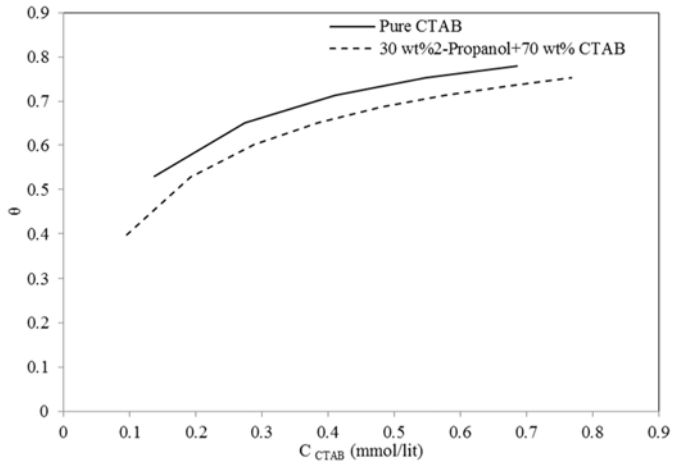

Fig. 8. The surface coverage of CTAB in terms of concentration of CTAB in the bulk liquid solution for the aqueous solution of pure CTAB and (30 wt%2-Propanol + 70 wt% CTAB).

The results of the previous section prove that both original in combination with Eq. (23) and Frumkin's model work well for pure CTAB and alcohols. Hence, these two models should be applied to the aqueous solutions of (CTAB + alcohols). Similar to the pure CTAB and alcohols, firstly, the surface tension measurements were conducted at the temperature of 298.15 K. All experiments were conducted for (90 wt% CTAB + 10 wt% alcohols), (80 wt% CTAB + 20 wt% alcohols), (70 wt% CTAB + 30 wt% alcohols), and (60 wt% CTAB + 40 wt% alcohols). The experimental surface tensions have been presented in Table 5. Table 6 reports the measured value of CMC. One can see that the addition of alcohols increases the values of CMC. The results show that when the percent of alcohols increases, the CMC of the (CTAB + alcohol) aqueous solution increases.

Figs. 5 and 6 compare the experimental data with the calculation results. This comparison shows that the Frumkin's model cannot predict the surface tension of the aqueous solutions of (CTAB+ alcohols). These results prove that the simplification of the Frumkin's model is in principle unsuitable for the aqueous solutions of (CTAB+ alcohols). Figs. 5 and 6 and the results in Table 5 prove that the original model in combination with Eq. (23) is a suitable model for the aqueous mixture of (CTAB+ alcohols). The lower values of AAD_γ show that this model has good predictions of the surface tension. The value of AAD_γ was 2.75 for this section.

The satisfactory prediction of the surface tension by the original model in combination with Eq. (23) allows us to compute the surface coverage. Surface coverage is a parameter that shows how absorption of CTAB can be affected in the presence of alcohols. Therefore, it is an important parameter. The values of surface coverage have been shown in Figs. 7 and 8.

The results of this part indicate that the surface coverage of CTAB decreases in the presence of the alcohols. Therefore, the presence of alcohols reduces the absorption of CTAB at the interface. This can be explained by the following discussion. In the pure water, surfactant tends to adsorb at the air–water interface in an oriented fashion due to the hydrophobic tails. This behavior is controlled by interactions between the tail group of CTAB and the water molecules. In the presence of an alcohol, the other interaction exists between the tail group and the molecule of an alcohol. Table 7 shows that this interaction is stronger than the one that exists between the tail group of CTAB and the water molecules. Therefore, the hydrophobic tail group is soluble in the aqueous solution of ethanol and the surface coverage of CTAB decreases. Such results and explanation can be found in [38], so the results of this study confirm the ones in [38].

The hydrophobic effects of the hydrophobic tail of surfactants can be considered as a main driving force of micelle formation [38]. Based on the obtained results, the interaction between the hydrophobic tail of CTAB and alcohols is stronger than the one between the water and hydrophobic tails. Therefore, the formation of CTAB micelle in the presence of alcohols is more difficult than the pure water. Moreover, the micelle formation is more difficult at the higher concentrations of alcohols.

Table 7
The interactions (a_{12}) between the tail group of CTAB and the molecule of alcohols, including 1-Propanol, 2-Propanol, and 1-Butanol by using the original model + Eq. (23).

System	a_{12}
(CTAB + 1-Propanol)	−1.367
(CTAB + 2-Propanol)	−1.463
(CTAB + 1-Butanol)	−1.500

5. Conclusions

The surface tensions for an aqueous solution of CTAB, 1-propanol, 2-propanol, and 1-butanol were measured by using the pendant drop method. The temperature and pressure of all experiments were 298.15 K and 1 bar, respectively. According to the equality of chemical potentials at the interface and aqueous solution, a model was used. The parameters of this model, including molar area, the surface-to-solution distribution constant, and interactions were computed for pure CTAB and alcohols. The surface tensions of these aqueous solutions were successfully reproduced. Then the surface tensions were measured for aqueous mixtures of (CTAB + alcohols) at different concentrations. Also, the CMC of the applied systems was determined based on the surface tension measurements. The parameters of the pure CTAB and alcohols were applied to the aqueous mixtures of (CTAB + alcohols). The applied model was used to predict the values of surface tension and surface coverage. This model successfully computed the surface tension for the aqueous solutions of (CTAB + alcohols). In the presence of alcohols, the surface coverage of CTAB decreased, and the values of the CMC increased.

List of symbols

a	Interaction parameter
AAD	average absolute deviation
b	surface-to-solution distribution constant
c	concentration
d_e	maximum diameter of the droplet
d_s	small droplet diameter
f	activity coefficient
g	gravitational constant
H	shape factor of a droplet
N_a	Avogadro number
R	ideal gas constant
T	temperature
V	molar volume
x	mole fraction

Greek letters

α	bulk phase
γ	surface tension
Γ	surface ecxess
θ	surface coverage
μ_i	chemical potential of component i
Π	surface pressure
ρ	density
Δ	difference
ω	molar area

Subscripts

b	bulk
c	critical
calc	calculation
exp	experimental
i,j	components i and j
S	surface
0	water
1	surfactant or additive

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