

Iranian Journal of Oil & Gas Science and Technology, Vol. 9 (2020), No. 3, pp. 26–43  
http://ijogst.put.ac.ir

## Experimental Measurement of Equilibrium Surface Tension of an Aqueous Solution of Polyethylene Glycol and a Surfactant

Fateme Beiranvand<sup>1</sup>, Hesam Najibi<sup>2\*</sup>, and Bahram Hashemi Shahraki<sup>2</sup>

<sup>1</sup> Ph.D. Candidate, Petroleum University of Technology Ahwaz, Iran

<sup>2</sup> Professor, Department of Gas Engineering, Petroleum University of Technology, Ahwaz, Iran

### Highlights

- An experimental setup for measuring equilibrium surface tension of solutions is designed and constructed.
- To show the reliability of the experimental setup, some data on pure water are measured and compared with the literature data, and good consistency is observed.
- The equilibrium surface tension of aqueous solutions of different surfactants (sodium dodecyl sulphate (SDS), Triton CG-110, dimethyl di-dodecyl-ammonium bromide (DDAB)) and polyethylene glycol with molecular weights of 200, 300, 400, and 600 and the equilibrium surface tension of ternary solutions of PEG–surfactant–water have been measured and reported.
- Redlich–Kister (RK) thermodynamic surface tension model has the lowest error in predicting the experimental data.

Received: August 21, 2019; revised: September 15, 2019; accepted: September 28, 2019

### Abstract

A device is designed and constructed for measuring the equilibrium surface tension of water and a number of other solutions. The measured equilibrium surface tension of water, as a reference fluid, has good consistency with literature data. Moreover, the equilibrium surface tension of the aqueous solutions of surfactants and polymer composed of sodium dodecyl sulphate (SDS), Triton CG-110, dimethyl di-dodecyl-ammonium bromide (DDAB), and polyethylene glycol (PEG) with different molecular weights of 200, 300, 400, and 600, as well as that of the ternary solutions of SDS/PEG/water, Triton CG-110/PEG/water, and DDAB/PEG/water at 293.15 K and atmospheric pressure are measured. The equilibrium surface tension of the aqueous solutions of PEG 600 are measured at 296.15 K because PEG 600 is solid at 293.15 K. The measured data are compared with the predictions of thermodynamic models, and the results show that Redlich-Kister (RK) model has the lowest error in predicting the experimental data.

**Keywords:** Equilibrium Surface Tension, Surfactants, Polyethylene Glycol, Thermodynamic Models

### How to cite this article

Beiranvand F, Najibi H, Hashemi Shahraki B, *Experimental Measurement of Equilibrium Surface Tension of an Aqueous Solution of Polyethylene Glycol and a Surfactant*. Iran J. Oil Gas Sci. Technol., Vol. 9, No. 3, p. 26–43, 2020.  
DOI: 10.22050/ijogst.2020.198631.1519

## 1. Introduction

The surface tension of a liquid mixture is an important physical property that plays a major role in the mass transfer at the interface. In the chemical industry, surface tension determines the quality of products such as coatings, paints, detergents, cosmetics, etc. and is effective in various production

\* Corresponding Author:

Email: hesamnajibi60@gmail.com, najibi@put.ac.ir

processes such as distillation, extraction, adsorption, and so on (Ivanov et al., 2016; Ozkan et al., 2010; Pan et al., 2018; Goussard et al., 2017; Khazaei et al., 2014). While the surface tension of pure liquids at various temperatures (ranging from their melting point to their critical point) are available for a large number of materials, data on chemical mixtures are extremely rare. Due to the importance of the surface tension, several thermodynamic models and empirical correlations are developed to predict its value for different solutions. The thermodynamic models are usually based on excess functions which are usually represented by the well-known Redlich-Kister (RK) polynomials (Redlich et al., 1948).

Jufu et al. (1986) presented a two-parameter equation based on the local composition concept proposed by Wilson for calculating the surface tension of liquid mixtures. This equation is obtained by modifying Hildebrand-Schütt equation (Hildebrand et al., 1987) for ideal two-component systems. One of the most popular models is the one presented by Marsh (Marsh, 1977). It is a general equation for calculating excess thermodynamic functions for different properties of aqueous solutions, including surface tension under isothermal equilibrium conditions. Sonawane and Kumar (1999) presented a model for predicting the surface tension of two-component fluid mixtures based on the Butler equation (Butler, 1932). This equation is one of the thermodynamic models widely accepted by engineers and researchers. In another work, Chunxi et al. (1964) derived a two-parameter equation for measuring the surface tension of two-/multi-component liquid mixtures based on the Wilson equation (Wilson, 1964) using the excess Gibbs free energy. Santos et al. (2003) also developed a model for calculating the excess surface tension of two-component fluid mixtures based on empirical and thermodynamic relations. Their model, which is derived from the Butler equation (Butler, 1932), also covers the model of Sonawane and Kumar (1999). Fanaei Khosroshahi et al. (2016) proposed a four-parameter equation based on the thermodynamic definition of surface tension using the Gibbs free energy. In fact, their proposed model is a modification of Chunxi's equation (Chunxi et al., 1964) for binary systems.

In the last two decades, aqueous solutions of polymers are widely used in separation processes (Annunziata et al., 2002; Chaiko et al., 1999; Chen et al., 2005). In this context, polyethylene glycol (PEG) is used to reduce the surface tension of surfactant aqueous mixtures (Karimi et al., 2012; Lu et al., 2005; Heydari et al., 2019; Chao et al., 2012; Yu et al., 2004). PEG is highly used for the reduction of surface tension in many industries, including oil, petrochemical, medical, pharmaceutical, and sanitary industries. It can also be added to firefighting foam to prevent it from dissolving in hydrocarbons. Therefore, understanding the surface tension of aqueous solutions of PEG as a function of its concentration and evaluating the effect of PEG on the surface tension of surfactant solutions are very the key to predicting the performance of PEG in such applications. To this end, we aim to study the behavior of polyethylene glycols and surfactants in aqueous mixtures. While the data on the surface tension and interface properties of pure liquid polymers are widely available in the literature, data on the surface tension of polyethylene glycol aqueous mixtures are extremely rare. Furthermore, the variations in the surface tension of surfactant–polyethylene glycol mixtures with concentration have not been studied so far. In this work, the equilibrium surface tension of the aqueous solutions of sodium dodecyl sulphate (SDS), Triton CG-110, dimethyl di-dodecyl-ammonium bromide (DDAB), and polyethylene glycol with different molecular weights of 200, 300, 400, and 600, as well as that of the ternary solutions of SDS/PEG/water, Triton CG-110/PEG/water, and DDAB/PEG/water at 293.15 K and atmospheric pressure are measured. It should be noted that the data on the equilibrium surface tension of the aqueous solutions of PEG 600 are measured at 296.15 K because PEG 600 is solid at 293.15 K. The measured data are also compared with the predictions of different thermodynamic models, and the results show that Redlich-Kister (RK) model has the lowest error in predicting the experimental data. The descriptions of the thermodynamic models are presented in Table 1.

Table 1

Surface tension thermodynamic models.

Author	Expression for $\sigma$ or $\sigma^E$	Parameters	Reference
Santos et al. (SFF)	$\frac{\sigma^E}{x_i x_j} = A + B(x_i - x_j)^c$	$A, B, \text{ and } C$	Santos et al., 2003
Sonawane et al. (SK)	$\frac{\sigma^E}{RT} = x_i x_j \left( \frac{1}{A_i^*} - \frac{1}{A_j^*} \right) (\delta_p + \delta_m x_j)$	$\delta_p$ and $\delta_m$	Sonawane et al., 1999
Jufu et al. (JBZ)	$\sigma = \sum_{i=1}^{N_c} \frac{x_i \sigma_i^*}{\sum_{j=1}^{N_c} x_j f_{ij}} - \frac{\sum_{i=1}^{N_c} \sum_{j=1}^{N_c} x_i x_j  \sigma_i^* - \sigma_j^* }{\sum_{q=1}^{N_c} x_q f_{iq} \sum_{r=1}^{N_c} x_r f_{jr}}$	$f_{ij}, f_{iq}, \text{ and } f_{jr}$	Jufu et al., 1986
Chunxi et al. (CWZ)	$\sigma^E = -RT \sum_{i=1}^{N_c} \left[ \frac{x_i}{\sum_{j=1}^{N_c} x_j \Lambda_{ij}} \sum_{j=1}^{N_c} x_j \left( \frac{\partial \Lambda_{ij}}{\partial A} \right)_{T,P,x} \right]$	$\Lambda_{ij}$ and $\left( \frac{\partial \Lambda_{ij}}{\partial A} \right)_{T,P,x}$	Chunxi et al., 1964
Redlich-Kister (RK)	$\sigma^E = x_i x_j \sum_{k=0}^p B_k Z_{ij}^k \quad z_{ij} = x_i - x_j$	$B_k$	Redlich et al., 1948
Marsh (M)	$\sigma^E = x_i x_j \frac{\sum_{k=0}^p B_k Z_{ij}^k}{1 + \sum_{l=1}^m C_l Z_{ij}^l} \quad z_{ij} = x_i - x_j$	$B_k$ and $C_l$	Marsh, 1977

## 2. Experimental procedures

### 2.1. Materials

The purity and suppliers of the chemicals used in our experiments are reported in Table 2. The solutions have been prepared by gravimetric method using a digital balance with the accuracy of  $\pm 0.0001$  g.

Table 2

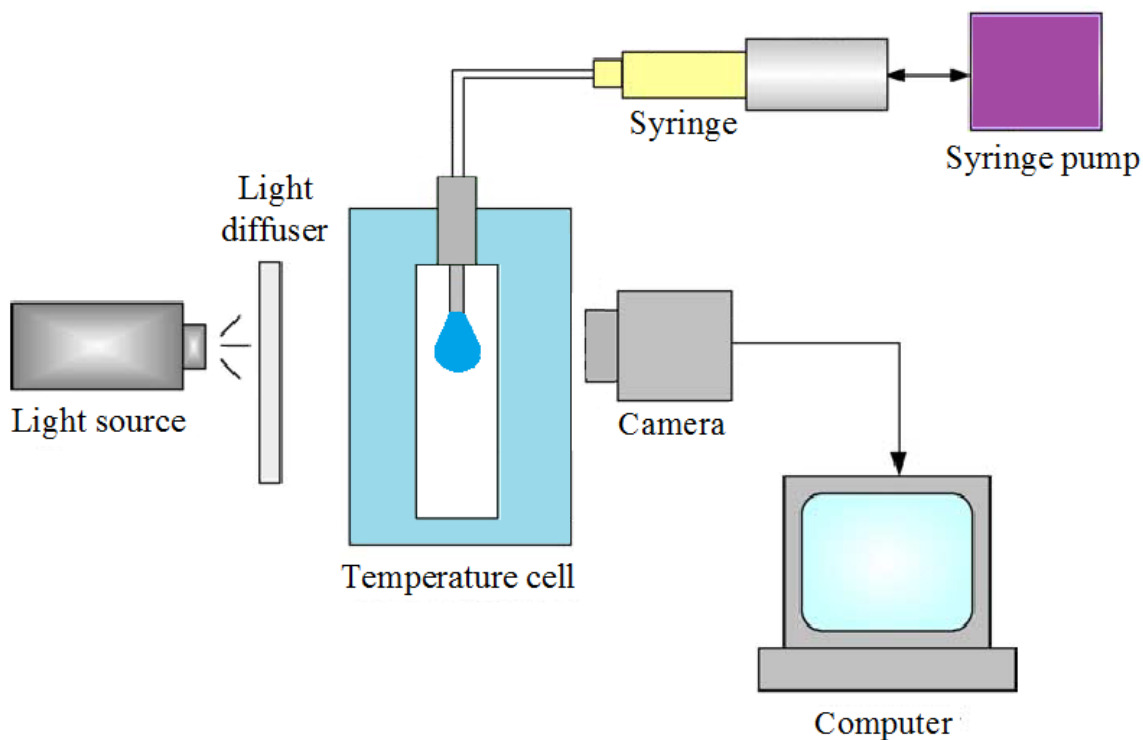
Purity and suppliers of chemicals.

Material	Purity (mass fraction)	Company
Sodium dodecyl sulfate (SDS)	0.95	Solar Bio
Dimethyl di-dodecyl ammonium bromide (DDAB)	0.98	Sigma Aldrich
Triton™ CG-110	-	Sigma Aldrich
PEG 200, 300, 400, 600	1.0	Samchun

### 2.2. Apparatus

A schematic diagram of the experimental apparatus used for the surface tension measurements in this work is shown in Figure 1. The pendant drop method is also used to measure equilibrium surface

tension, and a medical needle with a diameter of 0.0008 m is employed to drip the fluid. Briefly, this device includes a syringe pump, a camera, a syringe, an extension tube, a needle, a temperature cell, and a laptop. The syringe pump can move a piston of a  $10 \times 10^{-6} \text{ m}^3$  syringe at different speeds. The pump provides the desired flow rate by pushing the piston into the syringe and moving it. In all the tests, the flow rate of the surfactant was set at the lowest level so that it has time to penetrate into the air droplet and the equilibrium surface tension can be measured. A Dino-Lite AM 7115MZTW digital microscope camera with a resolution of  $2592 \times 1944$  pixels was used to capture the images of the droplets. The images of the syringe pump and camera are shown in Figures 2 and 3 respectively.



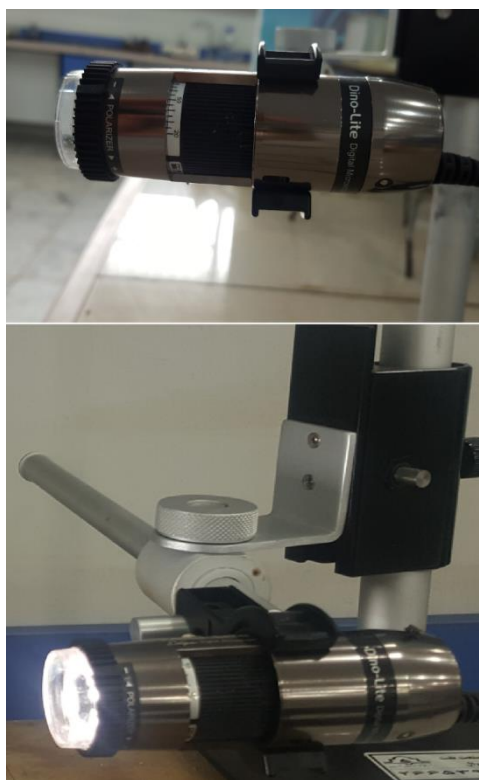
**Figure 1**

A schematic diagram of the experimental setup designed and assembled for surface tension measurements.



**Figure 2**

Programmable single syringe pump that holds one 10 cc syringe.



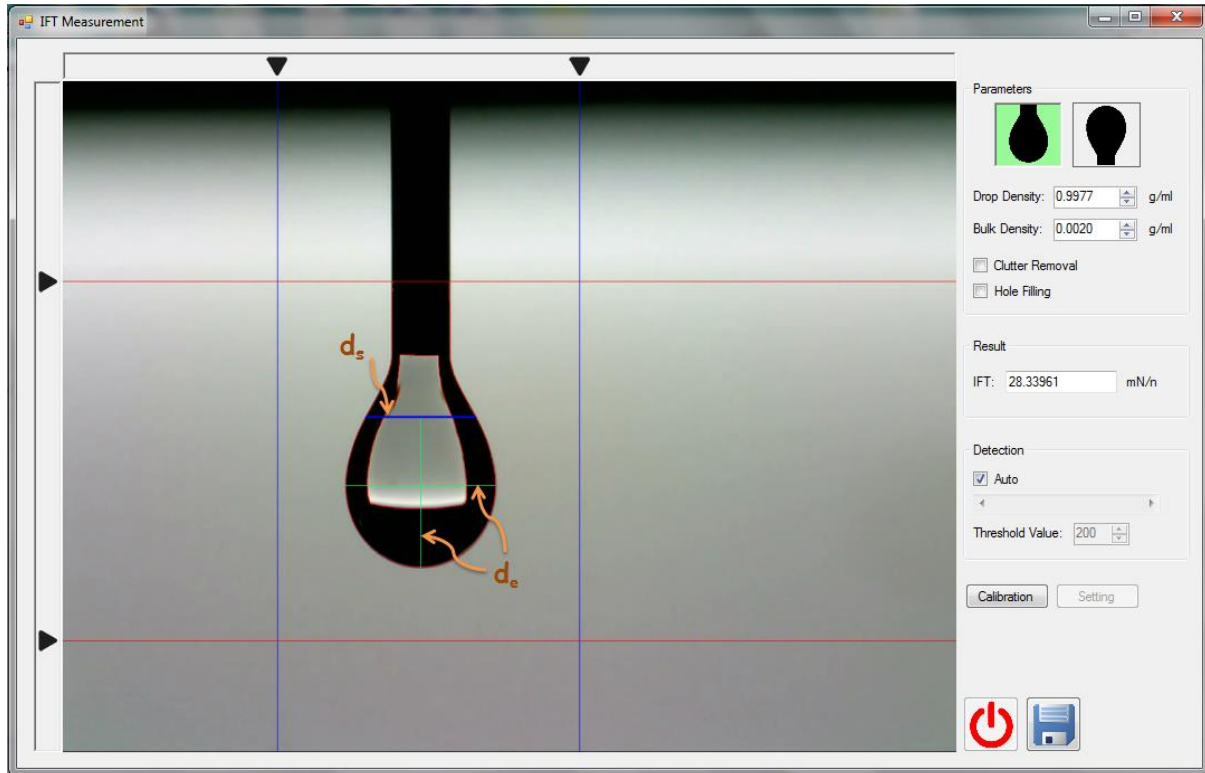
**Figure 3**

Dino-Lite AM 7115MZTW digital microscope camera with a resolution of  $2592 \times 1944$  pixels.

### 2.3. Experimentation

The required compositions of the aqueous solutions of the surfactant and polymer to be studied in this work were predicted using Design Expert software. All the solutions were prepared by a digital balance with the accuracy of  $\pm 0.0001$  g and a magnetic stirrer. The prepared solution was left intact in a glass jar for half an hour to remove all the produced bubbles, and then the solution was transferred to the syringe and extension tube very slowly. The needle was connected to the extension tube and was attached to the base with a clamp. The light source and camera were put in the correct distance, and the camera software was launched to capture clear images of the droplet. After ejecting a portion of the solution from the needle for ventilation, the pump flow rate was set at  $1.389 \times 10^{-11}$  m<sup>3</sup>/s to prolong the formation of the droplet sufficiently so that the surfactant molecules can attach onto the droplet surface and reach an equilibrium. After the speed of forming droplets became uniform, the equilibrium surface tension measurement started. To reduce the error, for each solution, the camera captured a movie of the formation of about 10 constitutive drops. Finally, from the captured movie, suitable pictures were extracted and fed to the image analyzer software to calculate the surface tension. Figure 4 shows the image of a typical droplet analyzed by the software. The software measures the maximum diameter ( $d_e$ ) and the diameter at the height ( $d_s$ ) and calculates  $S$  as the ratio of  $d_s/d_e$ . Since ratio  $S$  is a function of the physical properties of the liquid, this relation is used to calculate surface tension (Herd et al., 1992). The density of each sample was calculated by measuring the volume and mass of the sample. All the experiments were performed at 293.15 K and atmospheric pressure; however, the data on the equilibrium surface tension of the aqueous solutions of PEG 600 were obtained at 296.15 K because PEG 600 is solid at 293.15 K. By feeding the density of the solution and air to the software, the surface tension is calculated by considering the shape and size of the droplet. To verify the results of the software,  $S$  values of about 50 drops were measured, and by using these values, the surface tension of

each drop was calculated using Andreas method (Andreas et al., 1938). The calculated values were well in agreement with the results obtained from the software. The results of the comparisons for some samples are reported in Table 3. Experimental uncertainty is determined using the method given by the National Institute of Standards and Technology (NIST) (Taylor et al., 1994). The results reveal that the maximum combined standard uncertainty ( $u_c$ ) for the measured surface tensions in this work is 0.36. All the surface tensions ( $\sigma$ ) are reported in milli Newton per meter (mN/m) in this work.



**Figure 4**

A screenshot of the IFT software used for surface tension measurement by pendant drop method.

**Table 3**

Calculated (Andreas et al., 1938) and software-predicted values for the surface tensions of some samples.

Sample	Composition (ppm)	Predicted value (mN/m)	Calculated value (mN/m)
Water	pure	72.79	72.81
SDS aqueous solution	3000	39.43	39.51
DDAB aqueous solution	92.76	24.61	24.99
Triton CG-110 aqueous solution	3482	29.04	28.82

### 3. Results and discussion

#### 3.1. Water equilibrium surface tension measurements

To show the reliability of the experimental setup used to measure the equilibrium surface tension in this work, some data on pure water were measured at 293.15 K and atmospheric pressure. According to Table 4, the average value for these measurements was 72.79 mN/m which is quite comparable with the values reported in the literature (Gaonkar et al., 1987; Pallas et al., 1989; Harkins, 1949).

**Table 4**

Water surface tensions at 293.15 K reported in the literature.

Surface tension (mN/m)	Reference
72.94	Gaonkar et al., 1987
72.80	Pallas et al., 1989
72.78	Harkins, 1949

### 3.2. Surfactant–water equilibrium surface tension measurements

The surfactants chosen to be studied were SDS (an anionic surfactant), DDAB (a cationic surfactant), and TritonCG-110 (a nonionic surfactant). For each sample, the critical micellar concentration (CMC) was measured. To this end, the surface tensions of the surfactants were measured at different concentrations at a constant temperature of 293.15 K, and the measured values were plotted versus concentration. The concentration at which the slope of the diagram changes sharply is the CMC. At concentrations lower than the CMC, the surface of the solution molecules is not saturated with the surfactant molecules. Therefore; by increasing the concentration of the surfactant, the surface tension decreases. At concentrations higher than the CMC, since the surface of the solution molecules is saturated with the surfactant molecules, adding the surfactant does not have effect on the surface tension of the solution. Based on the measurements, the critical micellar concentration of DDAB, Triton CG-110, and SDS at 293.15 K are equal to 50, 2500, and 2500 ppm respectively.

The experimental and predicted values for the surface tensions of the aqueous solutions of SDS, DDAB, PEG 200, PEG 300, PEG 400, and PEG 600 with the average absolute relative deviation (AARD) and standard deviation (*SD*) are reported in Tables 5a, 5b, 6a, 6b, 6c, 6d respectively. As shown in Table 5a, empirical models, including Santos et al. (SFF), Marsh (M), and Redlich-Kister (RK) models, predict experimental data much better than the thermodynamic models such as those by Jufu et al. (JBZ) and Chunxi et al. (CWZ). This trend is almost repeated for DDAB as shown in Table 5b, which may be attributed to the asymmetric behavior of SDS or DDAB molecules in water as the empirical models are developed for asymmetric systems.

**Table 5a**Experimental and predicted values for the surface tensions of the SDS aqueous solutions by different models along with AARD and *SD* values.

Concentration (weight PPM)	$\sigma^*$ (mN/m) (Experimental)	$\sigma$ (mN/m) (RK model)	$\sigma$ (mN/m) (M model)	$\sigma$ (mN/m) (SFF model)	$\sigma$ (mN/m) (JBZ model)	$\sigma$ (mN/m) (CWZ model)
SDS						
200	69.01	68.88	68.95	69.06	66.85	66.63
300	65.98	66.19	66.16	65.63	64.29	64.12
500	60	60.03	59.76	60.17	59.52	59.47
700	54.1	54.15	54.08	55.61	55.22	55.29
1000	48.04	47.61	48.22	49.95	49.69	49.94
1800	41.95	42.16	41.64	40.78	40.85	40.97
2250	40	39.97	40.1	39.24	40.1	39.34
2500	39.5	39.5	39.5	39.5	39.5	39.5
AARD		0.0744	0.0492	0.4191	2.1204	6.7814
<i>SD</i>		0.0162	0.0093	0.1274	0.4948	1.1241

\* Combined standard uncertainty for the measured surface tensions is 0.36.

**Table 5b**

Experimental and predicted values for the surface tensions of the DDAB aqueous solutions by different models along with AARD and *SD* values.

Concentration (weight PPM) DDAB	$\sigma^*$ (mN/m) (Experimental)	$\sigma$ (mN/m) (RK model)	$\sigma$ (mN/m) (M model)	$\sigma$ (mN/m) (SFF model)	$\sigma$ (mN/m) (JBZ model)	$\sigma$ (mN/m) (CWZ model)
11.6	65.88	65.88	65.88	66.17	62.96	61.56
23.19	51	50.98	51	50.04	51.37	51.06
34.79	35.98	36.08	35.98	36.09	37.36	40.56
37.5	33.5	33.42	33.46	33.56	33.96	38.1
42.5	29.69	29.69	29.75	29.83	28.63	33.57
46.38	27.82	27.82	27.8	27.85	27.95	30.06
50	26.78	26.78	26.78	26.78	26.78	26.78
AARD		0.2278	0.2688	1.4222	1.9631	1.9684
<i>SD</i>		0.0555	0.0584	0.3268	0.4606	0.4496

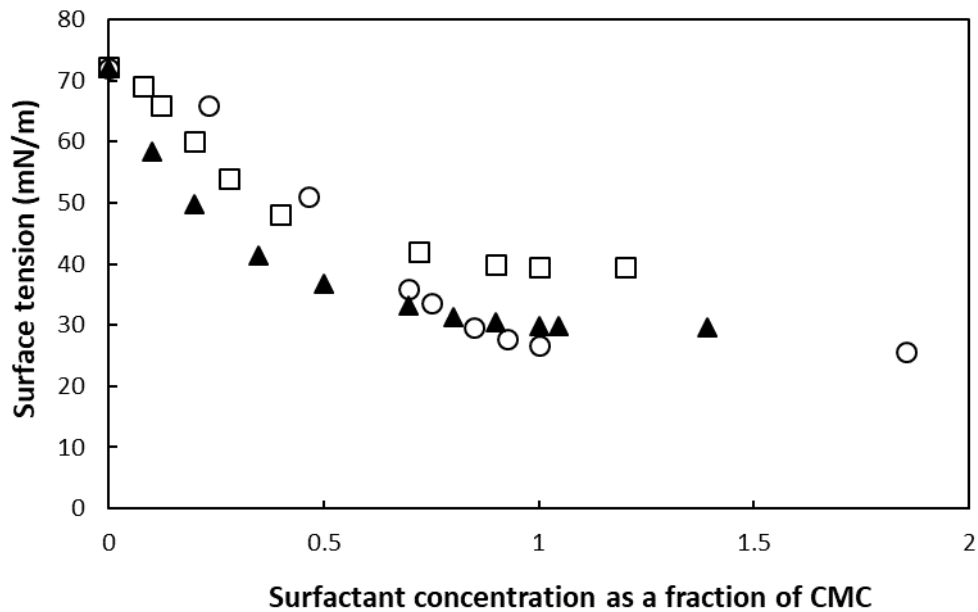
\* Combined standard uncertainty for the measured surface tensions is 0.36.

The variation in the measured equilibrium surface tensions of each surfactant aqueous solution as a function of concentration at 293.15 K is delineated in Figure 5. In this figure, the concentrations are reported as a fraction of the CMC. It is obvious that at concentrations lower than 1 CMC, the equilibrium surface tension of the aqueous solutions decreases by increasing the concentration of the surfactant, which is due to the migration of surfactant molecules to the air–solution interface. At concentrations higher than 1 CMC, the equilibrium surface tension of the solutions levels off because of the saturation of the surface of solution molecules with the surfactant molecules. The results of the surface tension measurements are compared with the predictions of the thermodynamic models mentioned in Table 1 for SDS and DDAB in Figures 6 and 7 respectively. Since Triton CG-110 is not a pure material, the prediction of the models for this compound is not possible. To complete the comparisons, the standard deviation and average absolute relative deviation for the different models are also calculated and presented in Tables 5a and 5b for SDS and DDAB respectively. As the results show, for both surfactants (SDS and DDAB), the Marsh (M) and Redlich-Kister (RK) models best fit to the experimental data. The two error-related parameters, namely *SD* and AARD, are calculated based on the following equations (Urđan, 2005):

$$SD = \left[ \sum_{i=1}^M \frac{(\sigma_{exp} - \sigma_{calc})^2}{M} \right]^{\frac{1}{2}} \quad (1)$$

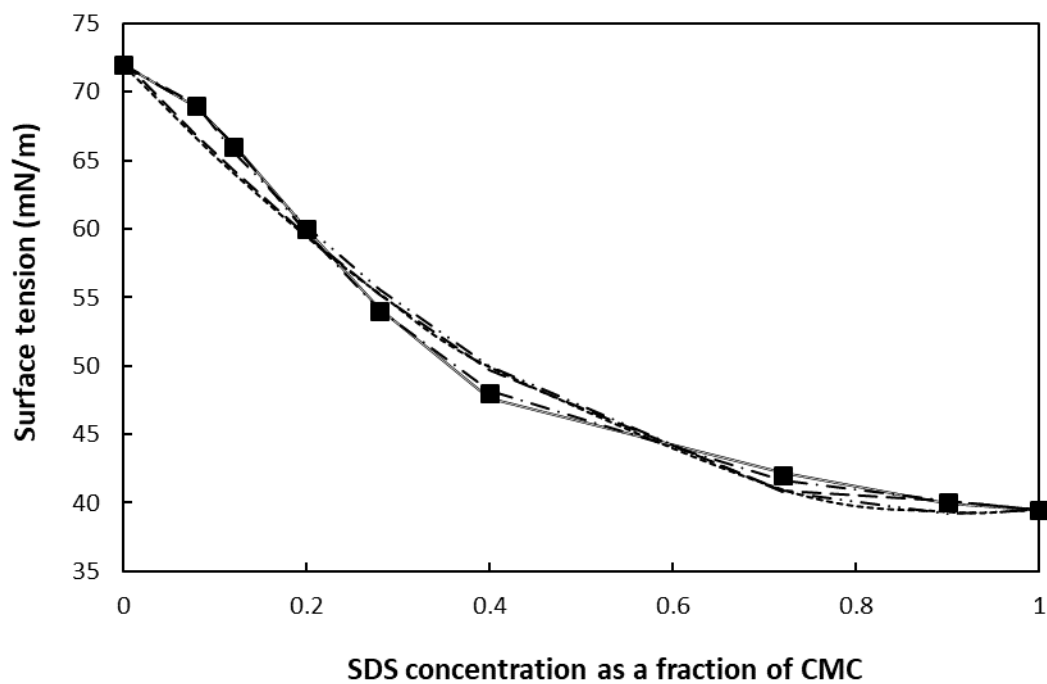
$$AARD(\%) = 100 \left[ \sum_{i=1}^M \frac{|(\sigma_{exp} - \sigma_{calc})/\sigma_{Exp}|}{M} \right] \quad (2)$$

where  $\sigma_{calc}$  and  $\sigma_{exp}$  are the calculated and experimental surface tensions respectively, and *M* represents the number of the data.



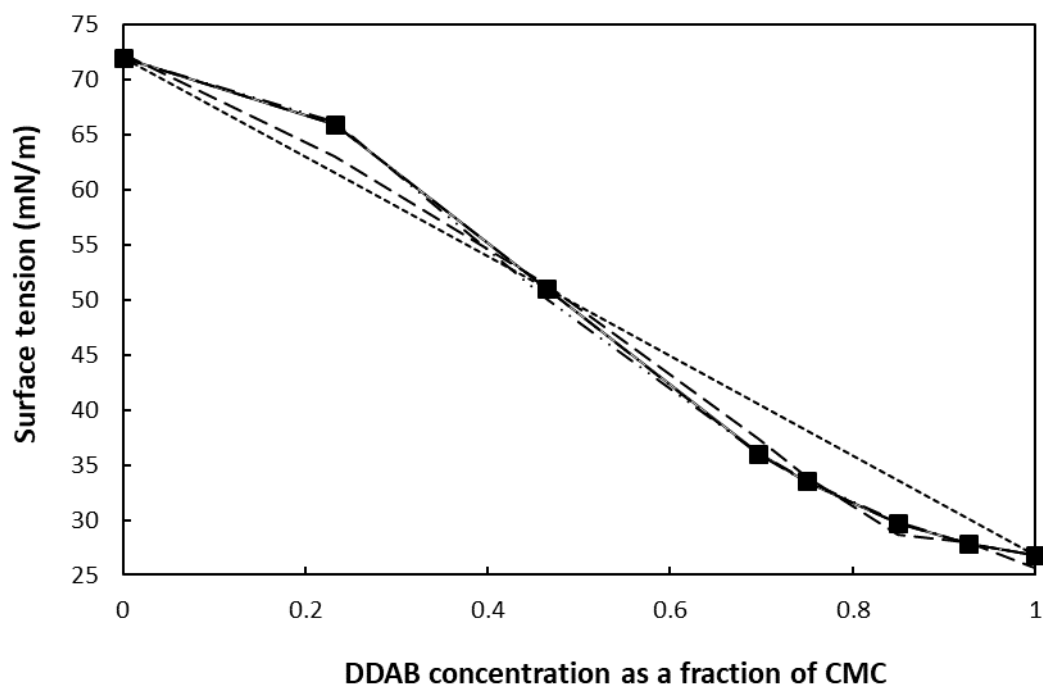
**Figure 5**

Experimental values for the equilibrium surface tensions of DDAB (○), Triton CG110 (▲), and SDS (□) aqueous solutions as a function of the concentration of the surfactants as a fraction of CMC.



**Figure 6**

Experimental and predicted values for the equilibrium surface tensions of the aqueous solutions of SDS: — : RK model (Redlich et al., 1948); ··· : SFF model (Santos et al., 2003); - - - : CWZ model (Chunxi et al., 1964); - · - · : JBZ model (Jufu et al. 1986); - - - - : M model (Marsh, 1977); ■ : Experimental data.

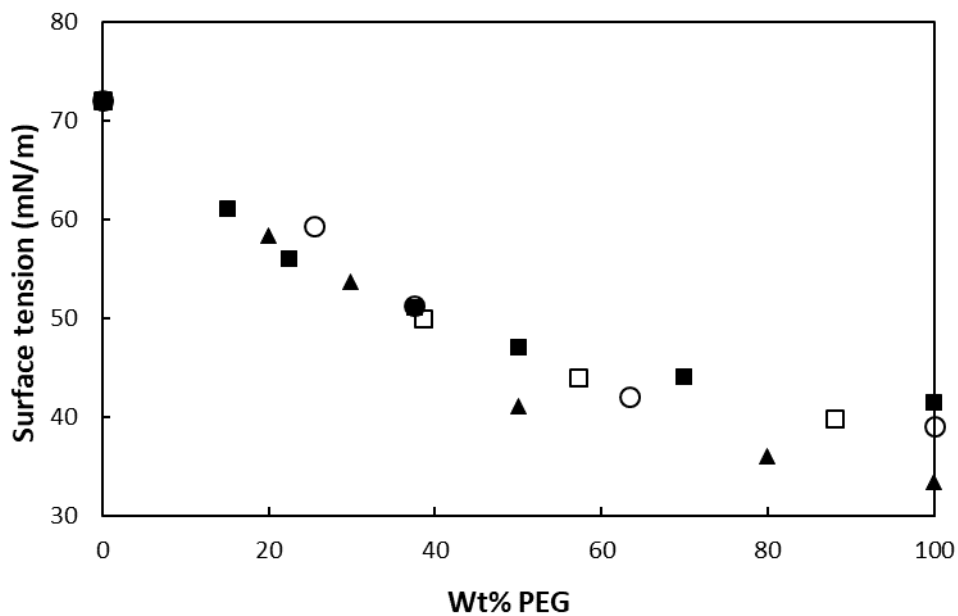


**Figure 7**

Experimental and predicted values for the equilibrium surface tension of the aqueous solutions of DDAB: — : RK model (Redlich et al., 1948); - · - : SFF model (Santos et al., 2003); - - - - : CWZ model (Chunxi et al., 1964); - - - - : JBZ model (Jufu et al. 1986); - · - : M model (Marsh, 1977); ■: Experimental data.

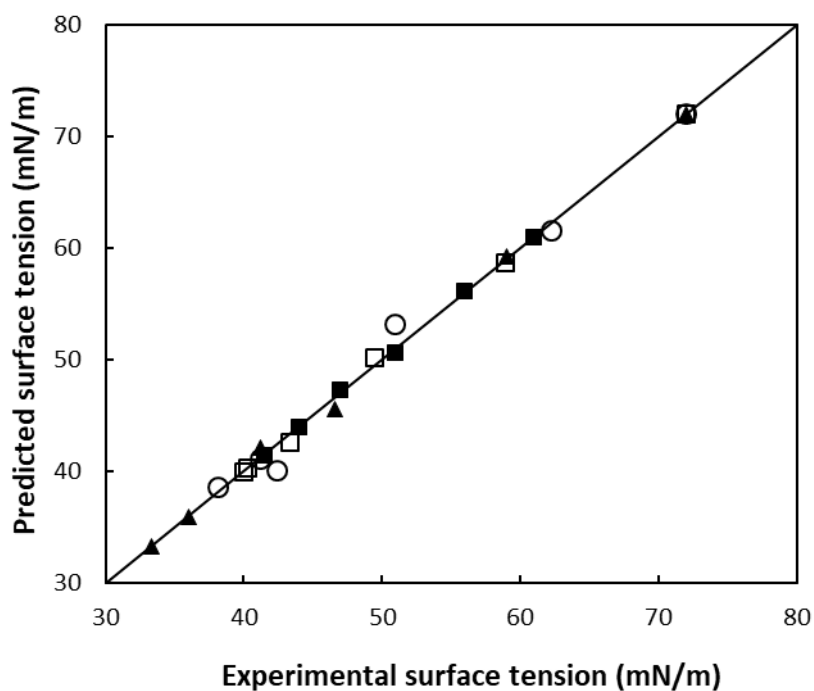
### 3.3. PEG–water equilibrium surface tension measurements

The variation in the measured equilibrium surface tension of the aqueous solutions of polyethylene glycol with molecular weights of 200, 300, 400, and 600 as a function of the weight percentage of PEG is depicted in Figure 8. The results show that the surface tension of the aqueous solutions of PEG decreases with increasing the concentration of PEG. At concentrations lower than 50 wt %, the surface tension drops more sharply, which may be due to the accumulation of PEG molecules at the interface between aqueous solution and air. The measured surface tensions of the aqueous solutions of polyethylene glycol with different molecular weights of 200, 300, 400, and 600 at various concentrations are compared with the predictions of RK, SFF, and CWZ models in Figures 9–11 respectively. The corresponding standard deviation and the average absolute relative deviation are calculated based on Equations (1) and (2) for these data and reported in Tables 6a–6d. The results show that RK model is more consistent with the experimental data, and, for most of the solutions, it has the lowest standard deviation and average absolute relative deviation among the three models.



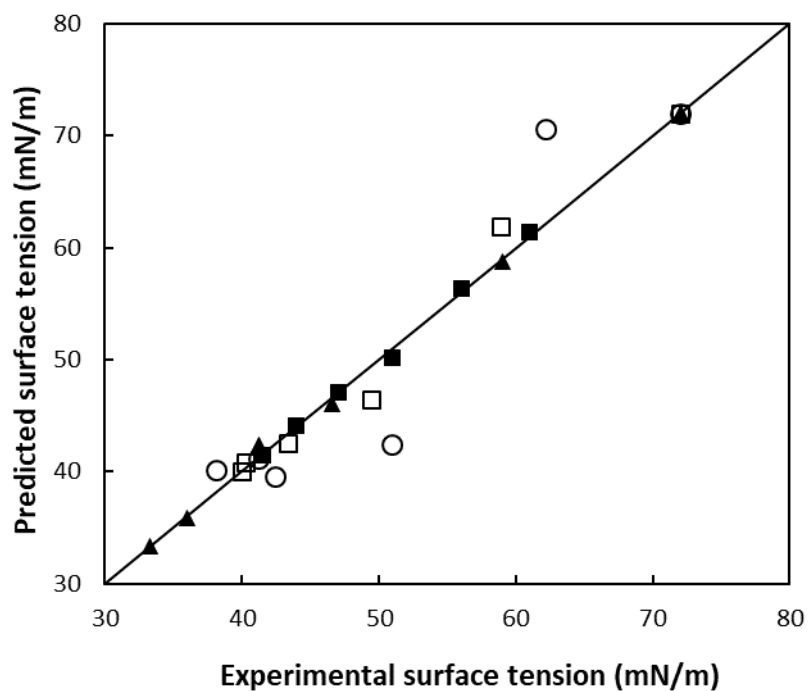
**Figure 8**

Experimental values for the equilibrium surface tensions of the PEG aqueous solutions versus the weight percentage of PEG: ■ PEG 200; ▲ PEG 300; ○ PEG 400; □ PEG 600.



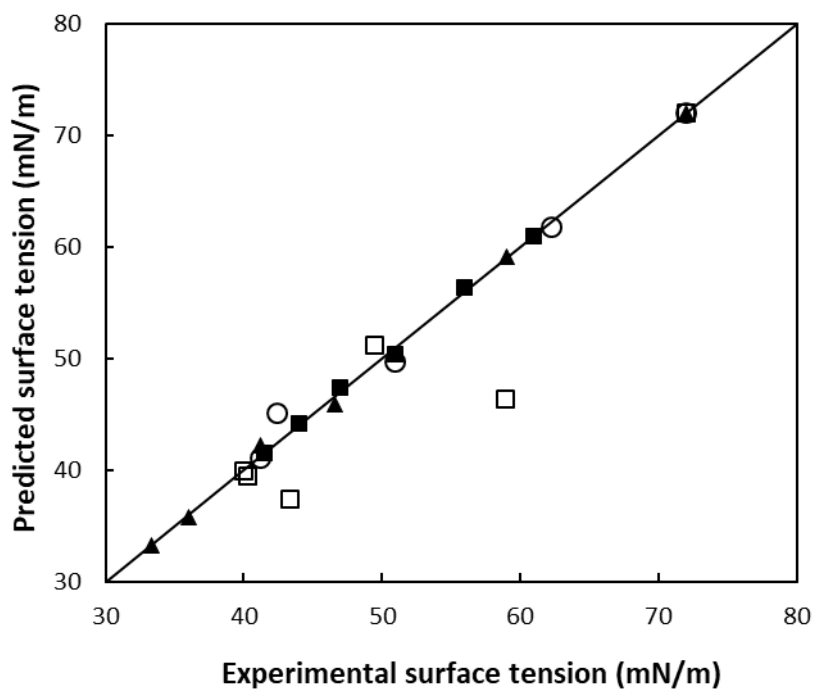
**Figure 9**

Predictions of RK model versus the experimental values for the equilibrium surface tension of the aqueous solutions of PEG: ■ PEG 200; ▲ PEG 300; ○ PEG 400; □ PEG 600.



**Figure 10**

Predictions of SFF model versus the experimental values for the equilibrium surface tension of the aqueous solutions of PEG: ■ PEG 200; ▲ PEG 300; ○ PEG 400; □ PEG 600.



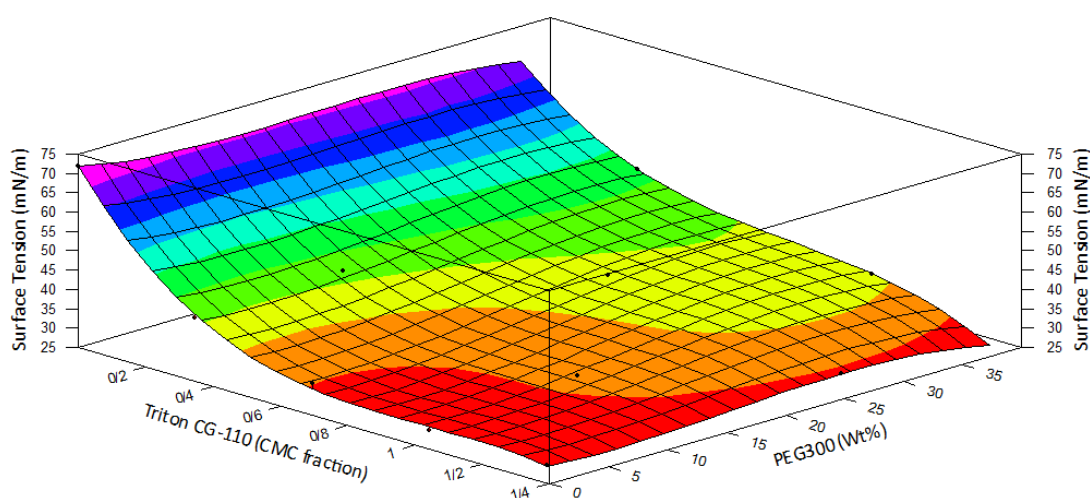
**Figure 11**

Predictions of CWZ model versus the experimental values for the equilibrium surface tension of the aqueous solutions of PEG: ■ PEG 200; ▲ PEG 300; ○ PEG 400; □ PEG 600.

### 3.4. PEG–surfactant–water equilibrium surface tension measurements

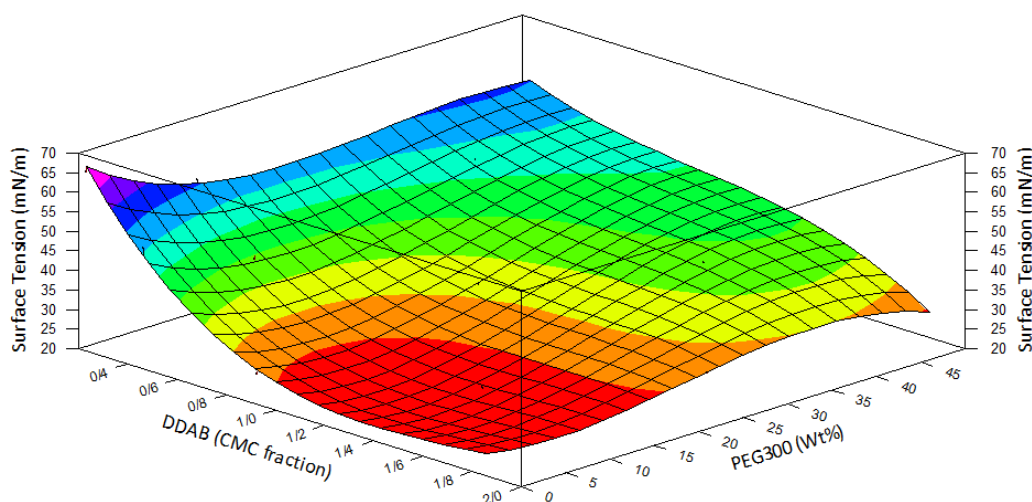
To measure the equilibrium surface tension of the ternary solutions of PEG, surfactant, and water, PEG 300 was chosen. The results of the laboratory measurements of these ternary solutions are presented in Figures 12–14. It is clear that the surface tension of the mixtures decreases with increasing the concentration of the surfactant but increases with an increase in the concentration of PEG 300, which may be due to the replacement of the surfactant molecules at the interface between aqueous solution and air with the PEG molecules.

Among the models presented in Table 1, only the models of Chunxi et al. (CWZ) and Jufu et al. (JBZ) can be used for the prediction of the surface tension of ternary solutions. Since the measured data in this work were not in the range of the data for which these models are developed, no model predictions for the ternary solutions are presented.



**Figure 12**

Experimental values for the equilibrium surface tensions of the aqueous solutions of Triton CG110 and PEG 300 versus the concentration of PEG and surfactant.



**Figure 13**

Experimental values for the equilibrium surface tensions of the aqueous solutions of DDAB and PEG 300 versus the concentration of PEG and surfactant.

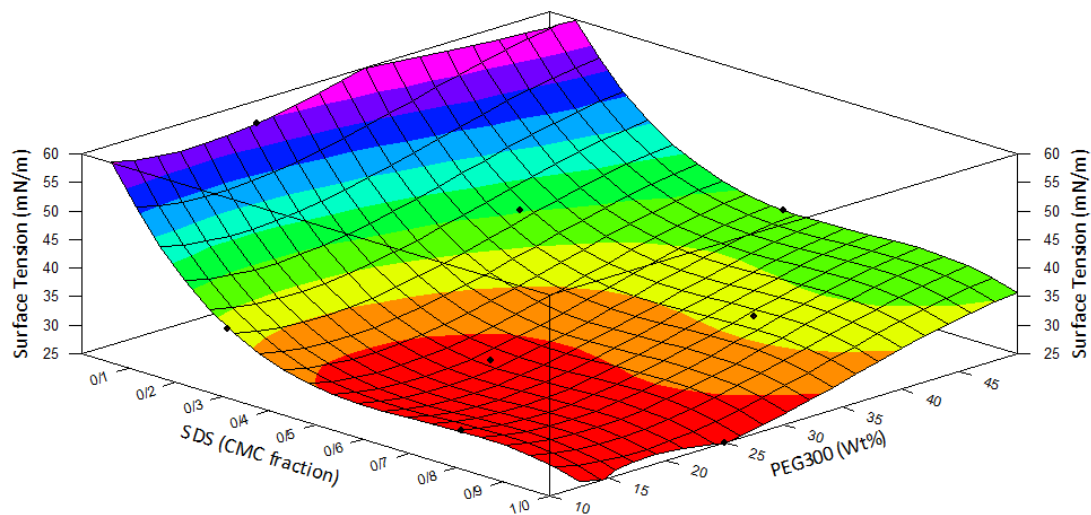


Figure 14

Experimental values for the equilibrium surface tensions of the aqueous solutions of SDS and PEG 300 versus the concentration of PEG and surfactant.

Table 6a

Experimental and predicted values for the surface tensions of the PEG 200 aqueous solutions by different models along with AARD and *SD* values.

Weight percent of PEG 200	$\sigma^*$ (mN/m) (experimental)	$\sigma$ (mN/m) (RK model)	$\sigma$ (mN/m) (SFF model)	$\sigma$ (mN/m) (CWZ model)
15	61.02	60.95	61.38	60.92
22.5	56	56.18	56.37	56.3
37.5	50.98	50.61	50.2	50.39
50	47.01	47.3	47.12	47.34
70	44.04	43.95	44.06	44.22
100	41.5	41.5	41.5	41.5
AARD		0.2706	0.4672	0.6202
<i>SD</i>		0.1744	0.2439	0.2664

\* Combined standard uncertainty for the measured surface tensions is 0.36.

Table 6b

Experimental and predicted values for the surface tensions of the PEG 300 aqueous solutions by different models along with AARD and *SD* values.

Weight percent of PEG 300	$\sigma^*$ (mN/m) (experimental)	$\sigma$ (mN/m) (RK model)	$\sigma$ (mN/m) (SFF model)	$\sigma$ (mN/m) (CWZ model)
20	59.04	59.23	58.69	59.11
40	46.62	45.55	46.06	45.86
50	41.23	42.18	42.38	42.18
80	36	35.93	35.83	35.75
100	33.32	33.32	33.32	33.32
AARD		0.857	0.8434	0.9507
<i>SD</i>		0.7256	0.3342	0.4147

\* Combined standard uncertainty for the measured surface tensions is 0.36.

**Table 6c**

Experimental and predicted values for the surface tensions of the PEG 400 aqueous solutions by different models along with AARD and *SD* values.

Weight percent of PEG 400	$\sigma^*$ (mN/m) (experimental)	$\sigma$ (mN/m) (RK model)	$\sigma$ (mN/m) (SFF model)	$\sigma$ (mN/m) (CWZ model)
20	62.18	61.59	70.6	61.81
40	50.9	53.22	42.46	49.73
60	42.37	40.17	39.57	45.11
80	38.15	38.63	40.09	44.56
100	41.17	41.17	41.17	41.17
AARD		1.9953	6.9694	1.561
<i>SD</i>		1.0971	3.099	1.0016

\* Combined standard uncertainty for the measured surface tensions is 0.36.

**Table 6d**

Experimental and predicted values for the surface tensions of the PEG 600 aqueous solutions by different models along with AARD and *SD* values.

Weight percent of PEG 600	$\sigma^*$ (mN/m) (experimental)	$\sigma$ (mN/m) (RK model)	$\sigma$ (mN/m) (SFF model)	$\sigma$ (mN/m) (CWZ model)
20	58.9	58.73	61.93	46.43
40	49.47	50.18	46.43	51.29
60	43.33	42.65	42.49	37.43
80	40.22	40.37	40.85	39.58
100	40	40	40	40
AARD		0.6121	2.467	6.6768
<i>SD</i>		0.3366	1.1043	3.4831

\* Combined standard uncertainty for the measured surface tensions is 0.36.

#### 4. Conclusions

PEG is used for the reduction of the surface tension in combination with surfactants in many industries. It is also added to firefighting foam to prevent it from dissolving in hydrocarbons. A device is designed and constructed to measure the equilibrium surface tension of water and a number of other solutions. To show the reliability of the experimental setup, some data on the surface tension of pure water are measured and compared with the literature data; good consistency is observed. The equilibrium surface tension of the aqueous solutions of different surfactants and polyethylene glycol with molecular weights of 200, 300, 400, and 600 was measured and reported in a wide range of concentrations. Some data on the equilibrium surface tension of the ternary solutions of PEG, surfactant, and water are also measured and presented. Further, the measured data are compared with the predictions of some thermodynamic models, and the results show that Redlich-Kister (RK) model has the lowest error in predicting the experimental data. Moreover, no thermodynamic model can predict the equilibrium surface tension of the ternary solutions of PEG, surfactant, and water. Therefore, it is suggested that a thermodynamic model that can predict the surface tension of these ternary solutions should be researched. Finally, due to the importance of using PEG in combination with surfactants in many different industries, the impact of PEG on the performance of surfactants needs further investigation.

## Nomenclature

A	Surface area
AARD	Average absolute relative deviation
$A_i$ and $A_j$	Surface parameters in CWZ model
CMC	Critical micellar concentration
DDAB	Dimethyl di-dodecyl-ammonium bromide
$d_e$	Maximum diameter
$d_s$	Diameter at the height equal to the maximum diameter
$f_{ij}$	Binary adjustable parameter
IFT	Interfacial tension (mN/m)
$P$	Pressure (atm)
PEG	Polyethylene glycol
$R$	Gas constant
$S$	Drop shape factor ( $S = d_s/d_e$ )
$SD$	Standard deviation
SDS	Sodium dodecyl sulfate
$T$	Temperature (K)
$x_i$	Mole fraction of component $i$
<b>Greek letters</b>	
$\Lambda_{ij}$	CWZ model parameters
$\sigma$	Surface tension
$\sigma_i^*$	Surface tension of pure component $i$
<b>Superscripts</b>	
$s$	Surface
<b>Subscripts</b>	
calc	Calculated value
exp	Experimental value
$i$	Component $i$
$ij$	Interaction of $i$ and $j$
$t$	Total

## References

- Andreas, J.M., Hauser, E.A., and Tucker, W.B., Boundary Tension by Pendant Drops, Fifteenth Colloid Symposium, 1938.
- Annunziata, O., Asherie, N., and Benedek, G.B., Effect of Polyethylene Glycol on the Liquid–liquid Phase Transition in Aqueous Protein Solutions, Proceedings of the National Academy of Sciences of the United States of America, Vol. 99, p. 14165–14170, 2002.
- Butler, J.A.V., the Thermodynamics of the Surface of Solutions, Proceedings of Royal Society a: Mathematical, Physical & Engineering Sciences, Vol. 135, p. 348–375, 1932.

- Chaiko, D.J., and Mego, W.A., a Method for Separating Water Soluble Organics from a Process Stream by Aqueous Biphasic Extraction, U. S. Patent US5948263A, 1999.
- Chao, Y.C., Su, S.K., Lin, Y.W., Hsu, W.T., Huang, K.S., Interfacial Properties of Poly Ethylene Glycol/Vinyl Tri Ethoxy Silane (PEG/VTES) Copolymers and Their Application to Stain Resistance, *Journal of Surfactants and Detergents*, Vol. 15, p. 299–305, 2012.
- Chen, J., Spear, S.K., Huddleston, J.G., and Rogers, R.D., Poly Ethylene Glycol and Solutions of Polyethylene Glycol as Green Reaction Media, *Green Chemistry*, Vol. 7, p. 64–82, 2005.
- Chunxi, L., Wenchuan, W., and Zihao, W., a Surface Tension Model for Liquid Mixtures Based on the Wilson Equation, *Fluid Phase Equilibria*, Vol. 175, p.185–196, 2000.
- Fanaei Khosroshahi, E., Heydari, A., Mirzayi, B., Shamkhali, A.N., a Model to Calculate Concentration Dependent Surface Tension of Binary Systems, *Fluid Phase Equilibria*, Vol. 423, p. 34–42, 2016.
- Gaonkar, A.G., and Neuman, R.D., the Uncertainty in Absolute Values of Surface Tension of Water, *Colloids and Surfaces*, Vol. 27, p. 1–14, 1987.
- Goussard, V., Duprat, F., Gerbaud, V., Ploix, J. L., Dreyfus, G., Rataj, V. N., and Aubry, J. M., Predicting the Surface Tension of Liquids: Comparison of Four Modeling Approaches and Application to Cosmetic Oil, *Journal of Chemical Information and Modelling*, Vol. 57, p. 2986–2995, 2017.
- Harkins, W.D., Weissberger, A., *Physical Methods of Organic Chemistry*, Vol. 1, p. 369, 1949.
- Herd, M.D., Lassahn, G.D., Thomas, C.P., Bala, G.A., and Eastman, S.L., Interfacial Tensions of Microbial Surfactants Determined by Real-Time Video Imaging of Pendant Drops, the SPE/DOE Eighth Enhanced Oil Recovery Symposium, p. 22–24, 1992.
- Heydari, N., Asgari M., Shojai Kaveh, N., Fakhroueian, Z., Novel Application of PEG/SDS Interaction as a Wettability Modifier of Hydrophobic Carbonate Surfaces, *Petroleum Science*, Vol. 16, p. 318–327, 2019.
- Hildebrand, M., and Schütt, S., Column Liquid Chromatography of the Novel Aldosterone Antagonist, *Journal of Chromatography*, Vol. 414, p. 217–222, 1987.
- Ivanov, Z., Karaivanova, M., Georgiev, D., and Georgieva, A., Study of the Effect of Surface Tension and its Influence on Specific Interfacial Area in Distillation Laboratory Column, *Science & Technologies*, Vol. VI, No. 4, p. 42–47, 2016.
- Jufu, F., Buqiang, L., and Zihao, W., Estimation of Fluid–Fluid Interfacial Tensions of Multi Component Mixtures, *Chemical Engineering Science*, Vol. 41, p. 2673–2679, 1986.
- Karimi, A., Fakhroueian, Z., Bahramian, A., Pour Khiabani, N., Babae Darabad, J., Azin, R., Aria, Sh., Wettability Alteration in Carbonates Using Zirconium Oxide Nano Fluids: EOR Implications, *Energy Fuels*, Vol. 26, p. 1028–1036, 2012.
- Khazaei, A., Parhizgar, H., and Dehghani, M.R., the Prediction of Surface Tension of Ternary Mixtures at Different Temperatures using Artificial Neural Network, *Iranian Journal of Oil & Gas Science and Technology*, Vol. 3, No. 3, p. 47–61, 2014.
- Lu, J.J., Yu, L.M., Cheung, W.W.Y., Goldthrope, I.A., Zuo, Y.Y., Policova, Z., Cox, P.N., Neumann, A.W., Poly(Ethylene Glycol) (PEG) Enhances Dynamic Surface Activity of a Bovine Lipid Extract Surfactant (BLES), *Colloids and Surfaces B: Bio interfaces*, Vol. 41, p. 145–151, 2005.

- Marsh, K.N., a General Method for Calculating the Excess Gibbs Free Energy from Isothermal Vapor–Liquid Equilibria, *Journal of Chemical Thermodynamics*, Vol. 9, p. 719–724, 1977.
- Ozkan, A., and Duzyol, S., Critical Solution Surface Tension for Liquid–Liquid Extraction, Separation and Purification Technology, Vol 76, p. 79–83, 2010.
- Pallas, N.R., and Pethica, B.A., The Surface Tension of Water, *Colloids and Surfaces*, Vol. 36, p. 369–372, 1989.
- Pan, S., Guo, R., Björnmalm, M., Richardson, J. J., Li, L., Peng, C., Zieschang, N. B., Xu, W., Jiang, J., and Caruso, F., Coating Super-Repellent to Ultralow Surface Tension Liquids, *Nature Materials*, Vol. 17, p. 1040–1047, 2018.
- Redlich, O., and Kister, A.T., Algebraic Representation of Thermodynamic Properties and the Classification of Solutions, *Industrial and Engineering Chemistry*, Vol. 40, p. 345–348, 1948.
- Santos, B.M.S., Ferreira, A.G.M., and Fonseca, I.M.A., Surface and Interfacial Tensions of the Systems Water N-Butyl Acetate Methanol and Water N-Pentyl Acetate Methanol at 303.15 k, *Fluid Phase Equilibria*, Vol. 208, p. 1–21, 2003.
- Sonawane, P.D., and Kumar, A., a New Equation for the Correlation of Surface Tension -composition Data of Solvent–solvent and Solvent–Fused Salt Mixtures, *Fluid Phase Equilibria*, Vol. 157, p. 17–28, 1999.
- Taylor, B.N., and Kuyatt, C.E., Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results, Adapted from NIST Technical Note 1297, 1994.
- Urdan, T.C., *Statistics in Plain English*, Psychology Press, 2<sup>nd</sup> Edition, 2005.
- Wilson, G.M., Vapor–Liquid Equilibrium. Xi. a New Expression for the Excess Free Energy of Mixing, *Journal of American Chemical Society*, Vol. 86, p. 127–130, 1964.
- Yu, L.M., Lu, J.J., Chiu, I.W.Y., Leung, K.S., Chan, Y.W., Zhang, L., Policova, Z., Hair, M.L., Neumann, A.W., Poly(Ethylene Glycol) Enhances the Surface Activity of a Pulmonary Surfactant, *Colloids and Surfaces B: Bio interfaces*, Vol. 36, p. 167–176, 2004.