Journal of Applied Chemistry **JAC**
http://chemistry.journals.semnan.ac.ir

Interfacial and micellization properties of pure surfactants with similar hydrocarbon chain length ($C_{16}H_{33}$) and different polar head in aqueous medium

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Article history:
Received:26/ Nov /2020
Received in revised form: 20/Jan/2021
Accepted: 14/Feb/2021

Abstract

The study of surfactant properties are significant for the production of pharmaceutical and anti-corrosion products, detergents and enhanced oil recovery. In the present work, the formation of micelles in different types of surfactants, *i*) cationic (cetyl pyridinium chloride, CPC, and cetyl trimethylammonium bromide, CTAB) and *ii*) non-ionic (Brij-C2, Brij-C12, Brij-C15 and Brij-C20) has been investigated in aqueous medium by tensiometric technique at 298.15 K. These surfactants (CPC, CTAB, Brij-C2, Brij-C12, Brij-C15 and Brij-C20) have the same hydrophobic chain length ($C_{16}H_{33}$) and different polar head groups. The major focus in this research is on the effect of polar head groups on critical micelle concentration (CMC), the standard free energy of micellization (ΔG_m^0), Gibbs adsorption energy (ΔG_{ads}^0) and some interfacial parameters, for example, surface excess concentration (Γ_{max}), minimum surface area per surfactant molecule (A_{min}), surface pressure at CMC (Π_{CMC}) and $pC_{20}(= -\log(C_{20})$. The results obtained show that the micellization properties of surfactants has more spontaneous and favorable conditions in nonionic structures. In Brij family surfactants, values of Γ_{max} and π_{cmc} at CMC point decreased with increasing the number of oxyethylene groups (or hydrophilic section) from Brij-C2 to Brij- C20. Also, increase in hydrophilicity of head groups of Brij series surfactants by more incorporation of oxyethylene groups enhanced their solubilization capacity in bulk solution.

Keywords: Micelle, hydrophilicity, Adsorption, CMC, Minimum surface area

1. Introduction

A surface-active agent is, as the name implies, a compound which will adsorb at an air-water or oil-water surface and at the interface of solids. Due to the dual nature of the surfactants, they self-aggregate in aqueous solution, and the simplest aggregated form is called micelle; the corresponding concentration is called the critical micelle concentration(CMC)[1-5].

For this behavior, surfactants are broadly used in detergency, drug delivery, separation processes, cosmetic products and so forth. The micelle and surface properties of surfactants depend widely on

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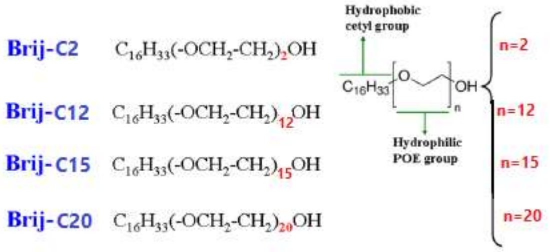
many factors such as pH, temperature, pressure and additives (added electrolytes and solvent type)[6−10]. Aggregation behaviors of different types of surfactants such as anionic, cationic, zwitterionic, nonionic and some gemini surfactants were widely studied in aqueous or non-aqueous solvents in the past few years[11-15]. Unfortunately, at present there is not enough published data to comparison of structure effects of different types of surfactants on their aggregation behavior (for example, comparison between ionic and non-ionic surfactants with same structures). It is thus important to look into different surfactant characteristics and study their relevant properties for practical applications. In the present work, the micelle formation of a homologous series of four non-ionic surfactant (Brij-C2, Brij-C12, Brij-C15 and Brij-C20) and two cationic surfactant (cetyl pyridinium chloride, CPC and cetyl trimethylammonium bromide, CTAB) was studied in aqueous medium using surface tension measurements at 298.15 K.

All the surfactants have same alkyl chain length (constituting 16 carbon atoms in the tail), but they differ in the size and type of the hydrophilic head group. There are 2, 12, 15 and 20 ethylene oxide linked with a cetyl moiety in Brij-C2, Brij-C12, Brij-C15 and Brij-C20, respectively; and there are pyridinium ions(Py^+) and trimethylammonium(TMA^+) linked with a cetyl moiety in CPC and CTAB, respectively. The general structure of six surfactants is illustrated in Fig. 1.



(CTAB) $C_{16}H_{33}N^+(CH_3)_3Br^-$

(CPC) $C_{16}H_{33}Py^+Cl^-$

Fig. 1. Molecular model of surfactants: Brij types and CPC.

The important parameters that affect the interfacial and micellization behaviors were investigated such as critical micelle concentration (CMC), free energy contribution to micellization (ΔG_m^0), Gibbs adsorption energy (ΔG_{ads}^0), Gibbs surface excess (Γ_{max}), minimum area per surfactant molecule (A_{min}), surface pressure at CMC(Π_{CMC}) and pC_{20} (or $-\log(C_{20})$ [1].

2. Experimental procedure

2.1. Materials

The non-ionic surfactants, polyoxyethylene (2) cetyl ether (Brij-C2, $C_{16}E_2$, n=2, HLB=5.3, MW=330 g. mol^{-1}) and polyoxyethylene(20) cetyl ether (Brij-C20, $C_{16}E_{20}$, n=20, HLB=15.7, MW=1124 g. mol^{-1}) with purity of 99 % was purchased from Croda Chemical Co. (USA) and used without purification. Cetyl pyridinium chloride (CPC) (99.5%) and cetyl trimethylammonium bromide(CTAB) (99%) was procured from Merck Company and recrystallized several times before use. All solutions were prepared with doubly distilled water.

2.2. Tensiometric measurements

The surface tension measurements of the surfactant solution have been performed by the platinum-iridium ring method with an automated Du Noüy tensiometer (model: Sigma 701, Finland).

). Before each set of experiments the surface tension of the deionized water was measured to control the calibration of the tensiometer. The determination of surface tension of water (or each sample) is very sensitive to impurities which might be present on the ring. For this purpose, prior to each measurement, the platinum ring was cleaned by using acetone followed by washing with double-distilled water and then it was heated briefly by holding it above a Bunsen burner until glowing. The reported value was an average of 7 records, where the maximum standard deviation from the average value was less than ±0.035 mN.m^{-1}. The instrument was connected to a LAUDA(model ECO RE415) circulating thermostat to maintain a constant temperature at 298.15 K with a precision of 0.1 K. For preparation of stock solutions of the surfactant, pure component was exactly weighed by an electronic balance with an accuracy of ± 0.0001 g (Sartorius, model BP121S, Goettingen, Germany).

The stock solutions of the surfactant were prepared in double-distilled water with known concentration (∼10 to 15 times the CMC concentration). The surface tension(σ) was measured after every addition of the concentrated solution of surfactant to the known volume of water (by Hamiltonian microliter syringe). During such measurements, the 5 min. time interval for equilibration was allowed after addition of the stock solution (for dilution) and thorough mixing. The CMC values were evaluated from the break points in the surface tension-log [surfactant] curves [5].

3. Results and discussion

3.1. Critical micelle concentration (CMC) of surfactants

Surface tension has provided one of the popular tools for investigating and understanding surface and bulk properties of solution. Reduction of surface tension in aqueous media depends on the replacement of surface water molecules by surfactant molecules of the bulk of the solution. For our purposes it is necessary to distinguish between the efficiency of a surfactant, measured by the concentration of surfactant required to produce some significant reduction in the surface tension of the water and its effectiveness, measured by the minimum value to which it can lower the surface tension, since these two often run counter to each other[16].

In this work, the surface tensions of Brij-C2, Brij-C12, Brij-C15, Brij-C20, CPC and CTAB aqueous solutions were measured at 298.15 K in order to estimate the surface and aggregation behavior of these components, and the measured data are presented in Table 1. Surface tension data of Brij C10 has been collected from literature [17].

Fig. 2 shows the surface tension curves (log scale) of surfactant aqueous solution at 298.15 K. The surface tension decreases initially with increasing concentration of components, indicating that the surfactant molecules are adsorbed at the air/solution surface. Then a plateau region with a nearly constant of slopes appears in the (σ−log[C]) plot, indicating that the stable micelles (or aggregate structures) have been formed. This figure shows that the surface tension values of surfactant aqueous solutions at this temperature follow the orders: CPC > CTAB> Brij-C20> Brij-C15 > Brij-C12 >Brij-C2 respectively, in the monomer and micellar regions.

Surface tension data of Brij-C12 and Brij-C15 have been reported in the literature, and in this work, the micellization parameters for two surfactants were estimated according to these results [18].

Table 1. Surface Tension of surfactant solutions (Brij-C2, Brij-20, CTAB and CPC) in aqueous media at different concentrations of components at T = 298.15 K and pressure 0.1 MPa. [a]

Brij-C2		*Brij-C20*		*CPC*		*CTAB*	
C(μM)	*σ*/(mN.m^{-1})	*C*(μM)	*σ*/(mN.m^{-1})	*C*(μM)	*σ*/(mN.m^{-1})	*C*(μM)	*σ*/(mN.m^{-1})
0	72.105	0	72.105		72.105	0	72.105
0.01	51.001	3.51	69.373	29.97	66.823	49.3	66.135
0.02	48.326	11.30	65.611	59.88	65.045	88.6	60.956
0.03	46.432	19.05	60.134	89.73	62.136	149	58.456
0.04	44.251	26.79	55.79	149.25	58.776	199.4	54.789
0.06	42.902	46.02	50.209	223.33	55.842	295.9	51.859
0.07	42.006	65.10	45.924	370.37	51.207	394.7	49.989

0.08	41.544	102.81	43.003	515.97	48.017	489.8	48.125
0.10	40.986	158.27	42.04	660.15	45.315	584.7	46.325
0.13	40.337	247.91	41.348	731.71	43.837	679.5	44.412
0.16	39.765	334.21	40.903	802.92	42.813	775.8	42.906
0.17	39.332	417.35	40.234	873.79	42.013	869.5	41.889
0.20	39.598	574.83	39.987	944.31	41.972	962.5	41.278
0.24	39.737	721.57	38.914	1014.49	42.096	1058.6	41.056
0.30	39.737	858.64	38.487	1153.85	41.927	1146.1	41.186
0.38	39.731			1830.99	41.841	1225.7	41.205
0.52	39.558			3094.17	41.417	1335.8	41.347
0.95	39.233			4248.93	40.976	1425.1	41.266
1.65	38.856			6284.58	40.737	1543.8	
2.77	38.634			8798.59	40.587		

[a] Standard uncertainties *u* are *u*(*T*) = 0.01 K, *u*(P) = 10 kPa and *u*(*x*) = 0.001.

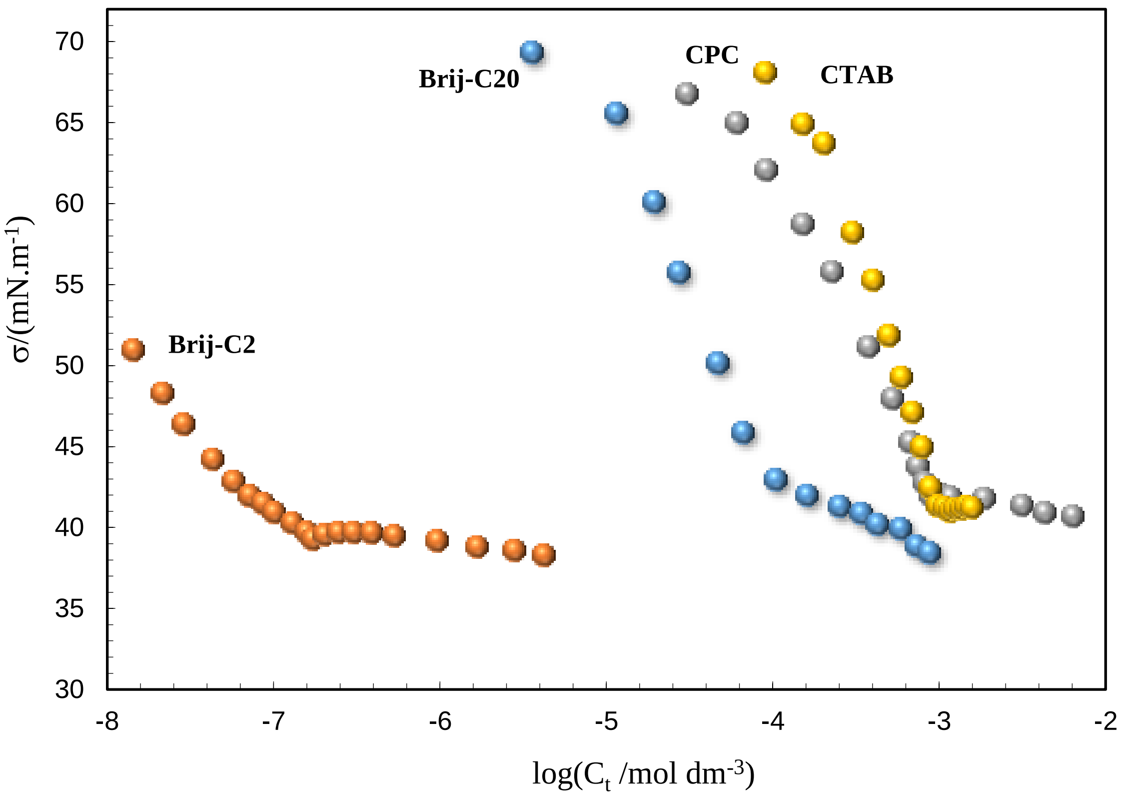


Fig. 2: Plot of surface tension against the Log[concentration] of surfactant in aqueous medium at 298.15 K.

Also, existence a small amount of impurity in the surface active-agent may make a specific minimum in plot of γ-log[surfactant] (see Brij-C2 plot). The impurities are more surface active than the surfactants and adsorb strongly in the air/liquid interface. Therefore, with increasing surfactant concentration, the decrease in surface tension is minimized and then with increasing surfactant concentration, due to the formation of micelles, they (micelles) begin to dissolve or remove impurities from the surface of the solution and the surface tension until a constant value increases. It was found that in the case of some non-ionic and ionic surfactants the minimum in the plot of surface tension can't be removed by more purification of the surfactants [19-20].

The CMC values and the surface tension at the CMC (γ_{CMC}) were estimated from the intersection of the two straight lines of the each curve in low and high concentration regions in surface tension curves (γ−log[C] curves) using a linear regression analysis method[21-22].

The determined critical micelle concentration were listed in Table 2. The changing head group of the surfactant from non-ionic (Brij-C2, Brij-C12, Brij-C15and Brij-C20) to cationic(CPC and CTAB) has an increasing on the critical micelle concentration(CMC) as the following order:

CMC (Ionic surfactant) > CMC (Non-ionic surfactant)

or

CTAB> CPC> Brij-C20> Brij-C15>Brij-C12> Brij-C2

As expected, cationic surfactants containing the charge on an ionic hydrophilic group show larger CMCs than those non-ionic surfactants (with the equivalent hydrophobic group($C_{16}H_{33}$)). This is described as being due to an increase in electrostatic self-potential of the surfactant ion when the ionic head group moves from the bulk water to the vicinity of the nonpolar micellar core during the process of micellization; work is required to move an electric charge closer to a medium of lower dielectric constant [1].

For the Brij series nonionic surfactants (in which the size of hydrophobic group is constant), the CMC in aqueous medium increases with increase in the number of OE segments in the polyoxyethylene chain. In this state, presumably due to the increasing hydrophilic character of the surfactant molecules, the migration of molecules occur with less tendency from the bulk solution to the interface and micelles are formed at higher concentrations (see Fig. 3).

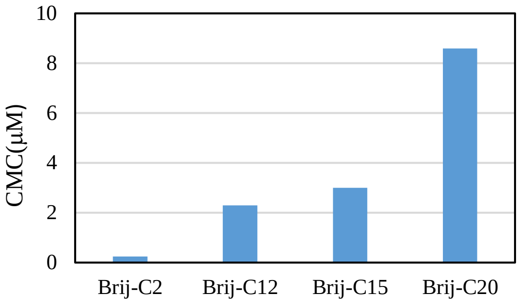


Fig. 3: Plot of critical micelle concentration, CMC, as a function of different types of Brij's at 298.15 K.

Comparison between CMC values for CPC and CTAB, in quaternary cationics in two components, CPC (due to pyridinium ion, py^+) has smaller CMC than the corresponding CTAB (due to trimethyl ammonium ion, $N^+(CH_3)_3$). This may be due to the greater ease of packing the planar py^+, compared to the tetrahedral $N^+(CH_3)_3$ group, into the micelle [1].

3.2. Adsorption of surfactant at the air-water interface

surfactants orientate at the air-water interface and decrease surface tension. The values of their adsorption per unit area of the surface at different concentrations can be estimated with the Gibbs adsorption equation[1, 23]:

$$d\pi = \sum_i \Gamma_i RTd \ln a_i \qquad (1)$$

Table 2. Micellar and surface properties of surfactants aqueous solutions at 298.15 K and atmospheric pressure.

Component	CMC	σ_{CMC}	π_{CMC}	pC20	Γ_{max}	A_{min}	ΔG^0_{mic}	ΔG^0_{ads}
	µM	mN. m	mN. m		µmol.m^{-2}	Å^2	kJ.mol^{-1}	kJ.mol^{-1}
CPC	963	42.01	30.10	3.45	2.19	75	-27.17	-40.92
CTAB	910	41.89	30.21	3.39	2.00	84	-27.31	-42.42
Brij-C2	0.25	39.73	31.33	7.85	2.61	63	-47.64	-59.64
Brij-C12	2.3	40.10	31.0	6.25	2.31	72	-42.14	-55.56
Brij-C15	3.0	41.51	30.1	5.91	2.05	81	-41.48	-56.16
Brij-C20	85.9	44.50	28.1	4.63	1.08	152	-33.16	-59.18

where dπ the change in surface pressure of the solvent (π is difference between surface tension of water and surface tension of surfactant solution), Γ_i is the surface excess concentration of any component of the system and a_i is the activity of the *ith* component, respectively (at temperature T).

The values of maximum surface excess($\Gamma_{\max}$) can be calculated from the following relation (in dilute solutions of surfactants(10^{-2} M or less) can be considered ideal behavior, a≈C)[23-24]:

$$\Gamma_{\max} = \frac{1}{2.303nRT}.\left(\frac{d\pi}{d\log C}\right)_{C\to CMC} \qquad (2)$$

where ((dπ/dlogC)) is the slope of the linear fit of the data before the CMC in the surface tension plots(closed to CMC), and *n* is the number of solute species (the value of *n* is equal to 1 in the nonionic surfactants, for example Brij and *n* is equal to 2 in the conventional ionic surfactants).

Also, and the minimum area per surfactant molecule at surface saturation, A_{min}, were calculated by the following equation[20, 24]:

$$A_{\min} = \frac{10^{20}}{\Gamma_{\max} N} \qquad (3)$$

In this equation, $\Gamma_{\max}$ is in mol.m^{-2}, and A_{min} is the in Å^2.

One of the important parameter which can be achieved from the surface tension data is pC20, which is defined as:

$$pC20 = -\log C20 \qquad (4)$$

In the above relation, C_{20} shows the required concentration of surfactant to cause a reduction of 20 mN·m^{-1} on the surface tension of water. In fact, pC20 is a parameter that shows the surface tension reduction efficiency of the surfactant.

The adsorption parameters obtained from surface tension measurements according above equations are summarized in Table 2.

Comparison of $\Gamma_{\max}$ and A_{min} values between CTAB and CPC shows that $\Gamma_{\max}$ for CTAB is lower than CPC, and correspondingly, the value of A_{min} became larger, this is due to the special structure of CTAB head group with the tetrahedral $N^+(CH_3)_3$ group. Increased charge repulsion among $N^+(CH_3)_3$ group in compared to py$^+$ (with similar alkyl chain length, $C_{16}H_{33}$) leading to increased values of A_{min} for CTAB molecule. Since the length of the alkyl chain is more important factor than the head group in reducing the surface tension, the surface tension and the surface pressure at CMC(σ_{CMC} and π_{CMC}) are slightly different for two cationic surfactants(CTAB and CPC).

In Brij family surfactants, values of $\Gamma_{\max}$ in below of the CMC decreased with increasing the number of oxyethylene groups (or hydrophilic section) from Brij-C2 to Brij- C20. From Table 2, it was obtained that A_{min} increased with decreasing of $\Gamma_{\max}$ and π_{cmc}.

This indicated that A_{min} depended mainly on the adsorption at interfaces, which in turn was affected by the total number of oxyethylene units and the effect of repulsive interactions between groups.

This trend indicated that the oxyethylene(OE) group number is important factor in determining these parameters. From other point view, the increase in $A_{\min}$ with OE number arises from the poorer packing at the interface since the hydrated, coiled chains sweep out a greater surface area as their lengths increase[25].

For Brij nonionic surfactants, the pC20 values decrease with increasing of POE number or increasing of hydrophilicity in surfactant(see Fig. 3).

This trend is linear for this surfactants with negative slope.

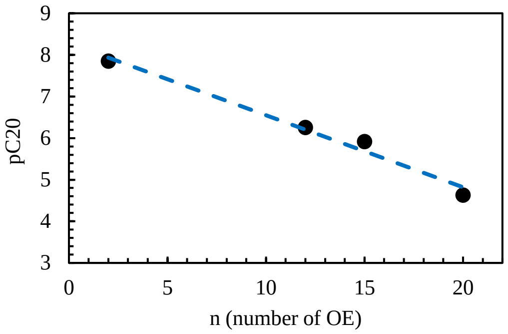


Fig. 3: Plot of pC20 (efficiency of surfactant adsorption at the interface) as a function of number of OE in Brij surfactants at 298.15 K.

The larger the value of pC20, the more efficiently the surfactant is adsorbed at the surface and the better efficiently it reduces surface tension, that is, the smaller the bulk liquid phase concentrations required either to gain saturation adsorption or to reduce the surface tension by 20 mN.m^{-1}. In among of Brij series, magnitude of pC20 for Brij-C2 is the highest value, indicating a high tendency of this surfactant for adsorption at the air-water surface relative to the inserting tendency in aqueous bulk medium.

Also, the result of Table 2 show that σ_{CMC} values are higher for shorter hydrophilic chains of Brij than the longer chains. This more surface activity in compounds with the short hydrophilic chain (example brij-C2) is due to the reduced solubility of these compounds in the aqueous medium and powerful tendency to migrate from the bulk to the interface.

3.3. Thermodynamic functions of Micellization and Interfacial Adsorption

The standard free energy of micellization per mole of monomer unit (ΔG^0_{mic}) of surfactants is related to the CMC by the following equation:

$$\Delta G^0_{mic} = RT \ln X_{CMC} \qquad (5)$$

Where X_{CMC} is the CMC value in mole fraction of surfactant unit in aqueous solution at the CMC (CMC/55.5), and other terms carry their usual meanings[26-27]. Table 2 summarizes the Gibbs energy values obtained by using Eq. 5 for the various surfactant solutions studied. The values of ΔG^0_{mic} are negative for all of the considered surfactants, which means that the micellization is a spontaneous process. Meanwhile, the mean standard free energy of micellization of non-ionic surfactant was more favourable than the micelle formation for ionic surfactant. This manifests that the micellization in ionic surfactants is more unstable due to stronger repulsive interactions between positive heads groups in micelle.

The standard free energy of interfacial adsorption (ΔG^0_{ads}) at the air-water interface of micelle has been estimated from the equation[28]:

$$\Delta G^0_{ads} = \Delta G^0_{mic} - \frac{\pi_{CMC}}{\Gamma_{\max}} \qquad (6)$$

Where $\Gamma_{\max}$ and π_{CMC} are the maximum surface excess and surface pressure at the CMC, respectively. ΔG^0_{ads} is the driving force for surfactant adsorption.

Table 2 summarizes the ΔG^0_{mic} and ΔG^0_{ads} values obtained by using Eqs. 5-6 for the studied surfactants. All obtained ΔG^0_{mic} and ΔG^0_{ads} values for six surfactants in the solution were negative. This indicates that the formation of surface monolayer and micelles is thermodynamically spontaneous.

In terms of ΔG^0_{mic} and ΔG^0_{ads}, the cationic surfactants (CPC and CTAB) are almost equally spontaneous, whereas for non-ionic Brij surfactants are comparatively more negative and more spontaneous.

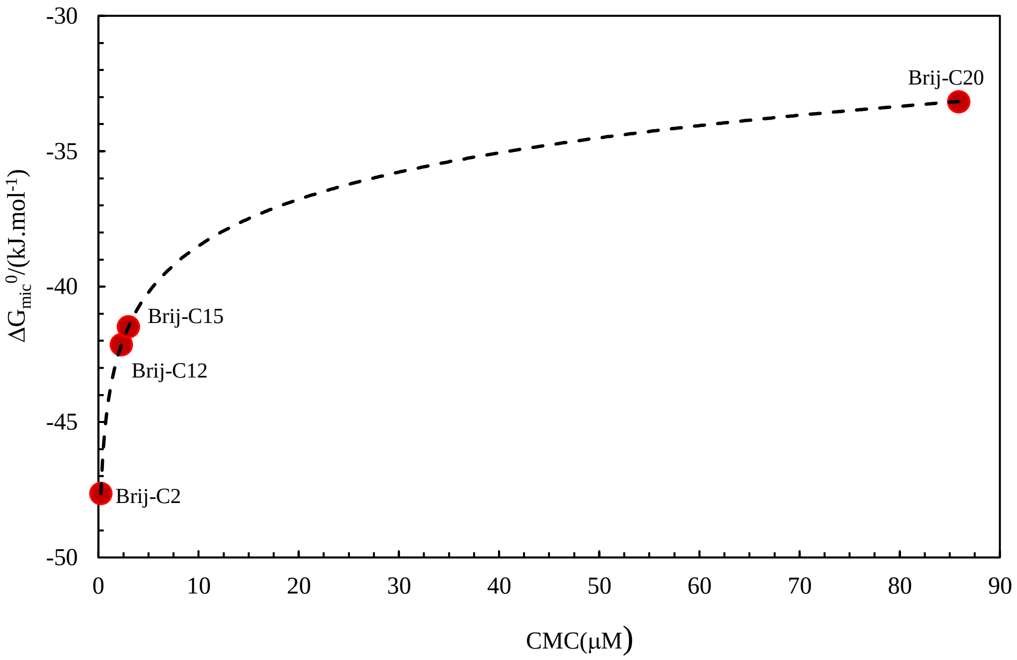


Fig. 4: Plot of the Gibbs energy of micellization (ΔG^0_{mic}) as a function of the critical micelle concentration of Brij surfactants. The symbols refer to the CMC obtained from surface tension data, and the continuous dashed curve is a guide for the eyes.

Fig. 4 shows the variation of ΔG^0_{mic} with CMC for the Brij surfactants. The values of ΔG^0_{mic} increase (towards less negative values) with increasing the CMC (or OE group number), and finally reaches approximately to the maximum level close to -34 kJ.mol^{-1}. This trend indicates that the formation of micelles in the presence of larger hydrophilic group is less spontaneous than those in the presence of smaller hydrophilic group.

This trend indicates that in a system with larger hydrophilic group, the process of micelle formation is less spontaneous and less favorable (due to stronger repulsive interactions between the bulky methyl groups in micelles). From the other point of view, in the studied Brij, the process of micelle formation is more spontaneous in a system in which the CMC value of component is lower.

The ΔG^0_{ads} values are completely negative in all surfactants. The magnitude of ΔG^0_{ads} is greater than that of ΔG^0_{mic}, indicating that the latter to be less favorable due to the hydrophobicity of surfactants, which leads them into the water-air interface. It is deduced that adsorption into interface is a primary and favorable process compared to micelle formation, which is a secondary and less favorable process.

These studies can be useful for selection of effective antifoams in different industrial. Foaming has been a major problem in the different industries, dating back to the early operation of the world plants where the need to control foaming with an antifoam agent was first identified. Ease of handling and solution preparation is also important. The physical properties of concern are surface properties, viscosity, freezing point, and flash point. Nonionic surfactants have the advantage over the more conventional antifoams of being highly soluble in water at ambient conditions. Thus solutions can be prepared without concern of phase separation. Moreover, freezing of nonionic surfactants in transit or during storage does not cause deterioration of the antifoam properties after thawing is complete which is unlike conventional antifoams [29].

4. Conclusion

Interfacial and micellization behaviors of six surfactants in two categories, ionic (CPC and CTAB) and non-ionic(Brij-C2, Brij-C12, Brij-C15 and Brij-C20) with similar alkyl chain length was studied by the tensiometric method. The effect of head groups of different surfactants on the micelle formation and molecular interaction determined quantitatively by various models. The following conclusions can be drawn from the work:

1- The experimental results indicates that the mean CMC value of ionic surfactants is greater than the mean CMC value of non-ionic surfactant in aqueous medium. Also, comparing CMC between CTAB and CPC shows that it is a higher value for CPC.

2- The results obtained show that $A_{\min}$ increased and $\Gamma_{\max}$ decreased with increasing the OE groups number in Brij structure

3- The efficiency of the surfactant adsorption at air-water interface (pC20) decreases with increasing in the number of OE units in the polyoxyethylene chain from Brij-C2 to Brij-C20..

4 The negative values of ΔG^0_{mic} and ΔG^0_{ads} in the all surfactants demonstrate that the micelle formation and surfactant adsorption at interface are spontaneous process, respectively.

5- In addition, it was found that the adsorption of surfactant at the air-water interface more favorable than the micelle formation(or $\left|\Delta G^0_{mic}\right| < \left|\Delta G^0_{ads}\right|$).

Acknowledgments

We gratefully acknowledge the financial support received for this research work from the Research Council of Semnan University.

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