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Study on surface properties of sodiumdodecyl sulfate and dodecyltrimethylammonium bromide mixed surfactants and their interaction with dyes

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Abstract

The antagonistic as well as synergetic interaction for dodecyltrimethylammonium bromide (DTAB) and sodiumdodecyl sulfate (SDS) mixed surfactants by using surface tension are investigated on the basis of the results obtained earlier, the efficiency of adsorption (pC_{20}), aggregation number (N), $\Gamma/\Gamma_{\max}$, effective Gibbs free energy ($\Delta G_{\text{eff}}^{\circ}$) and $\frac{CMC}{C_{20}}$ are calculated additionally with three different temperatures at $T = 293.15$, 298.15 and 303.15 K as the detailed surface properties. The binding constants and standard free energy change of SDS and DTAB mixture with the interaction of (2.5×10^{-5} mol L⁻¹ of methyl orange, MO and methylene blue, MB) are carried out by using UV-Vis spectroscopy at room temperature by using different models. The closer values of the binding constants and standard free energy change for SDS and DTAB mixture with the interaction of MO and MB are included in our investigations.

Keyword: Physical chemistry

1. Introduction

Mixed surfactants are widely used in our daily life and various industrial productions as compared to the single surfactants. Mixed surfactants have exclusive properties like, lower critical micelle concentration (CMC), higher surface activities, lower surface energy and lower critical aggregation concentrations (CAC) which are significant for detergency applications [1, 2]. Thus, the determination of the interactive performance of catanionic mixtures in the aqueous system is abundant prominence for scientific uses as organic and physical chemistry, mineral processing, petroleum, pharmaceutical, food science, cosmetics and biological industry [3, 4, 5, 6, 7, 8, 9, 10]. These surfactants are also used widely as capping agents to control the morphology of nanoparticles [11].

Therefore, the cationic and anionic mixed surfactants are induced fascinating microstructures not formed by the single surfactants like vesicles and rod-like micelles [12]. The thermodynamic and physicochemical properties are essential characteristics for understanding the primary and application prospects of the mixed surfactants solution [13, 14], like the formation of CMC, CAC and counterion binding, aggregation numbers, etc. which depends on the temperatures and presence of other molecules, salts, dyes, and biomolecules.

Mixed surfactants have appeared in extraordinary consideration because of their transportation abilities, high efficiency of solubilization and dispersion of drugs and other bioactive molecules [15, 16, 17]. Cationic and anionic surfactants mixtures are very significant for application, and their operations can be harmonizing in micellization induce the decrease of the CMC and surface energy mixture.

Earlier researchers have been reported on the interaction of cationic and anionic mixed surfactants by using thermodynamic, physicochemical and spectroscopic studies at single and different temperatures [18, 19, 20, 21, 22, 23]. Chauhan et al. [24] have been reported on the effect of co-solute on the micellisation of cationic and anionic mixed surfactants system at different temperatures in the aqueous and non-aqueous systems. Khan et al. [25] have been studied on the aggregation and thermodynamic behavior of amphiphilic imipramine hydrochloride and anionic surfactants in the aqueous system at different temperatures. Mola et al. [26] have been investigated the mixed micelle formation between tetradecyltrimethylammonium bromide and benzyldimethylhexadecylammonium chloride in the absence as well as the presence of urea using the experimental and theoretical technique. Kumar et al. [27] have been studied on the interaction between promethazine hydrochloride drug and sodiumdodecyl sulfate at different temperatures to see the monomeric and micellar phases of aqueous solutions of mixed systems in absence and presence of urea by conductivity methods. Malik et al. [28] have been reported the drug delivery vehicles, the mixed interfacial, as well as micellar behavior of the

sodium salt and bile salts mixtures in aqueous/electrolyte solutions through surface tension methods.

In this regard, Malik et al. [29] have been investigated the interaction of anionic bile salts sodium taurocholate and the anionic anti-inflammatory drug sodium salt of ibuprofen in aqueous solutions with urea using tensiometric and fluorometric techniques at 298.15 K. Bhattarai et al. [30] have been studied the interactions of cationic-rich and anionic-rich with water and methanol-water mixtures separately and found the reduction in surface tension through mixed micelle formation [31].

Hines et al. have been reported the theoretical assessment of micellisation of the mixed surfactant system [32]. Sohrabi et al. have been described the phase behavior and aggregate structures of mixtures of the oppositely charged surfactants cetyltrimethylammonium bromide and sodiumdodecyl sulfate [33].

In this study, we have investigated the effect of temperatures on the surface properties of SDS-rich and DTAB-rich in the aqueous medium at 293.15, 298.15 and 303.15 K in the depth such type of study is not reported yet. The resulting data have been discussed in terms of the interactions operating in between opposite charged based surfactants in the aqueous system including the effect of temperatures on the micellization of these surfactants.

Our first objective is to study the nonideality of mixed micellization at $T = 293.15$ K and determine the surface properties as the efficiency of adsorption (pC_{20}), aggregation number (N), effective Gibbs free energy ($\Delta G_{\text{eff}}^{\circ}$), the relation between (A_{min} and π_{cmc}), $\frac{\Gamma}{\Gamma_{\text{max}}}$ and $\frac{\text{CMC}}{C_{20}}$ of SDS-rich and DTAB-rich in an aqueous medium at $T = 293.15$ – 303.15 K.

Our second objective is to obtain the binding constants and standard free energy change of SDS and DTAB mixture with the interaction of (2.5×10^{-5} mol L⁻¹ of methyl orange, MO and methylene blue, MB) by using UV-Vis spectroscopy.

Earlier researchers have been analyzed the effect of dyes with mixed surfactants in the aqueous and non-aqueous solvent medium [34, 35, 36, 37, 38, 39, 40]. Samiey et al. [41] have been explained the rate constant of alkaline fading of crystal violet was measured in the presence of non-ionic (TX-100), cationic (DTAB) and anionic (SDS) surfactants at 283–303 K. Dey et al. [42] have been reported the fluorescence correlation spectroscopic study of dyes with SDS and DTAB. Thus, the dye-surfactant studies are applicable in the industrial, chemical research and dye separation processes [43, 44]. Tunç et al. [45] have been analyzed the absorption spectra of dye-surfactant mixtures show that dye-surfactant aggregates occur in the pre-micellar region. Zaghbani et al. [46] have been reported on the interactions of anionic dye Eriochrome Blue Black R (EBBR) with different cationic micelles of surfactants n-alkyl trimethyl ammonium bromide C_nTAB ($n = 12; 14; 16$ and 18)

have been investigated spectrophotometrically at 25 °C in pre-micellar and post-micellar region. There is no such work reported yet on the spectroscopic study of MO and MB with SDS-rich and DTAB-rich mixed surfactants system of using two different models as in this paper.

2. Materials and methods

2.1. Materials

The DTAB, SDS, MO, and MB were obtained from Sigma-Aldrich and SD Fine Chemicals Ltd. (Mumbai, India). The detail specification of chemicals is mentioned in Table 1. DTAB and SDS have the tendency to absorb the moisture; the vacuum desiccator filled with P₂O₅ was utilized for their storage.

2.2. Methods

The same solvent as Milli-Q water was used for making solutions of mixed surfactants at three different temperatures as described in the earlier study [18]. Similarly, Milli-Q was used for making the aqueous solutions of MB and MO (2.5×10^{-5} mol L⁻¹) in the airtight volumetric flasks.

2.3. Density and surface tension measurements

The densities (ρ) were noted by using the same density meter and procedure as used in the previous study [18]. The instrument was calibrated with DMSO at $T = 293.15$, 298.15 and 303.15 K, and check the performance of the instrument and the density values were found in compliance with that of the literature values, reported in Table 2 [47]. Density has been an average of three replicate measurements with $\pm 1.10^{-3}$ kg m⁻³ uncertainty in density. The surface tension was measured by using Survismeter [48] through pendant drop number (PDN) methods. The temperature was controlled by Lauda Alpha RA 8 thermostat with ± 0.05 K. After attaining a thermal equilibrium, the PDN was counted with an electronic counter. The Survis-meter was washed and cleaned with a similar procedure described in the previous

Table 1. Specification of chemicals used in this work.

Name of Chemicals	Purity ^a	M _w	Source	CAS No.
DTAB	~99 %	308.34	Sigma-Aldrich	1119-94-4
SDS	~98.5 %	288.37	Sigma-Aldrich	151-21-3
Methyl orange	>85 %	327.33	S.D. fine chemicals (Mumbai, India)	547-58-0
Methylene blue	>96%	319.85	S.D. fine chemicals (Mumbai, India)	122965-43-9

Purity^a as provided by suppliers, Dodecyltrimethylammonium bromide (DTAB), Sodiumdodecyl sulfate (SDS), Methylene blue (MB), Methyl orange (MO).

Table 2. Comparison of measured densities values (ρ) and Surface tension (γ) values of DMSO at $T = 293.15, 298.15$ and 303.15 K with literature data.

Temperature (K)	$\rho/10^3 \text{ kg m}^{-3}$		$\gamma/\text{mN}\cdot\text{m}^{-1}$		$\Delta\rho$	$\Delta\gamma$
	Exp.	Lit [47].	Exp.	Lit [49].		
293.15	1.100103	1.10073	43.41	43.36	−0.000627	0.05
298.15	1.095079	1.09574	42.78	42.70	−0.000661	0.08
303.15	1.090043	1.09074	42.12	42.05	−0.000697	0.07

Standard uncertainties are $u(T) = \pm 0.01$ K, $u(p) = \pm 0.01$ MPa.

Unit: $\Delta\rho = 10^3 \text{ kg m}^{-3}$, $\Delta\gamma = \text{mN}\cdot\text{m}^{-1}$.

$\Delta\rho = \text{Exp.} - \text{Lit.}$, $\Delta\gamma = \text{Exp.} - \text{Lit.}$ values.

study [18]. The noted surface tension is the average values of three repeated measurements with $\pm 0.03 \text{ mN m}^{-1}$ combined uncertainties in surface tension. The Survisometer was calibrated by using DMSO. The surface tension data of our system well agree with the literature value (Table 2) [49]. The presented surface tension (γ) and log C (i.e., C is the surfactant concentration) plotted, for calculating the CMC value.

2.4. Conductance measurements

Specific conductance data was measured at 293.15, 298.15 and 303.15 K with the Pye-Unicam PW 9509 model conductivity meter having the frequency of 2000 Hz using a dip-type cell with a cell constant of 1.15 cm^{-1} with an uncertainty of 0.01%. The instrument cell was calibrated by using the proposed method [50] using the aqueous potassium chloride solution. The temperature of the measurement cell was controlled with a Lauda Alpha RA 8 thermostat with ± 0.05 K.

2.5. UV-visible spectroscopy

Absorbance was measured by the Spectro 2060 plus model of UV-visible spectrometer. The spectral analysis was done in the range of 200–600 nm at 298.15 K. All UV-visible measurements were carried out with the following procedure. Firstly, the measurement of baseline with water was done, after that 3 ml of DTAB-rich and SDS-rich different concentrations of surfactant solutions involved obtaining a well-marked absorption band. For mixed surfactants interaction with dyes, the baseline was registered for given DTAB-rich solution, and afterward, a constant volume of aqueous methyl orange (MO) or methylene blue (MB) solution was added, and the solution was adequately mixed for 5 minutes after that absorbance was noted.

By experimental data, the intensity of dye absorbance as a function of the concentration of DTAB-rich was examined. The binding constants and standard free energy change of dyes with mixed surfactants were calculated.

3. Results and discussion

3.1. Stability and structural homogeneity assessment

From 0.000096 to 0.012 mol L⁻¹ SDS-rich and 0.000864–0.00504 mol L⁻¹ DTAB-rich mixed surfactants solution remains stoichiometrically active to induce an effective, stable surfactants mixture at 3:1 ratio. While with >0.012 mol L⁻¹ SDS-rich and >0.00504 mol L⁻¹ DTAB-rich mixed surfactant stoichiometrically is outnumbered that tends to precipitate with decreases the stability of mixed surfactants solution with stronger cohesive forces (Fig. 1).

Specific conductance analysis is directly related to the number of ions which is present in the solution; the higher is the ion concentration with higher is the specific conductance. Specific conductance furnishes us with information related to ionic association and the relative solvation ability of solvents with the ions. An inclusion of 0.000864 and 0.00504 mol L⁻¹ DTAB into aq-SDS solution, the % change of specific conductance values is very less (Fig. 2). It depicted that the ionic species could not be deviated while with >0.00504 mol L⁻¹ DTAB into aq-SDS solution, the higher % change is obtained (Fig. 2), it indicates that due to the charge neutralization of the ionic species the molecules could be aggregated. There is the chance of precipitation of DTAB-SDS combinations. So, one needs to make one component is in excess in comparison with another, then stable mixed micelles are formed. Moreover, the same trend obtained in SDS-rich mixed surfactants solution (Fig. 3). So we have chosen such a concentration range of DTAB and SDS because these were suitable for equal distribution with higher stability of molecular mixtures. It is mathematically represented as:

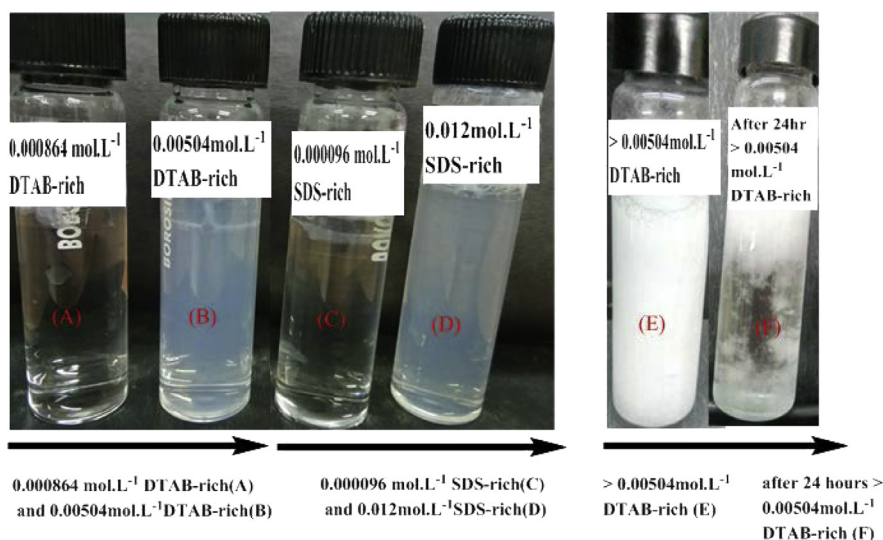


Fig. 1. The stability of DTAB-rich (Fig. A-B), SDS-rich (Fig. C-D) and >0.00504 mol L⁻¹ DTAB-rich (Fig. E-F) mixed surfactants solution.

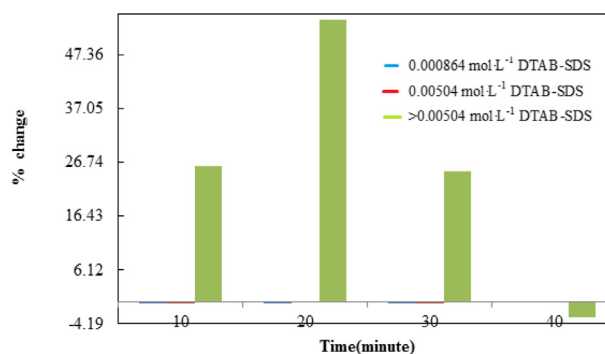


Fig. 2. The % change of conductance for 0.000864 to 0.00504 mol L⁻¹ DTAB-rich and > 0.00504 mol L⁻¹ DTAB-rich mixed surfactants solution.

$$\text{Stability domain} \int_{\text{SDS}=0.000096 \text{ mol} \cdot \text{L}^{-1}}^{\text{SDS}=0.012 \text{ mol} \cdot \text{L}^{-1}} \text{Homogeneous mixture of SDS} \\ \text{— rich mixed surfactant}$$

$$\text{Stability domain} \int_{\text{DTAB}=0.000864 \text{ mol} \cdot \text{L}^{-1}}^{\text{DTAB}=0.00504 \text{ mol} \cdot \text{L}^{-1}} \text{Homogeneous mixture of DTAB} \\ \text{— rich mixed surfactant}$$

3.2. Synergetic effect

Mixed aggregation is a fundamental property in the surface chemistry. The aggregation process of mixed surfactants molecules takes place by the most significant surface tension reduction of water [51]. The mixed CMC may be useful in detergency applications, and the used for controlled drug release, micro reactors and model membranes [52, 53, 54].

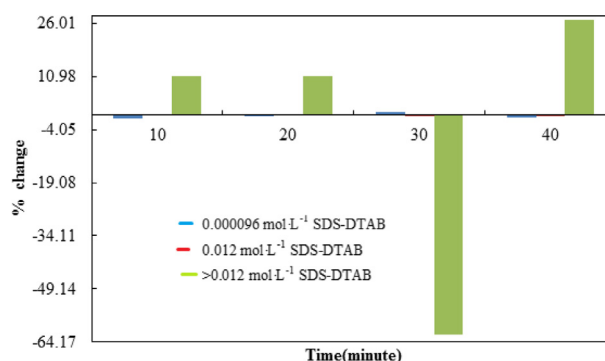


Fig. 3. The % change of conductance for 0.000096 to 0.012 mol L⁻¹ SDS-rich and > 0.012 mol L⁻¹ SDS-rich mixed surfactants solution.

In several cases of catanionic systems, the complex was seen and then generally insoluble in water; such systems have less application because of their structural interaction activities. Some cationic-anionic combinations have a high possibility to get precipitate through charge neutralization at a comparable ratio. The stable mixed micelles are formed when there is one component in excess [25, 26]. This study is interesting for mixed surfactants as cationic rich and anionic rich in the equimolar ratio (3:1) of mixing and the stability of the mixture of anionic and cationic surfactant has been established.

The analysis of experimental measured, mixed CMC is essential to compare with the different models. It was observed from the study that the CMC value of mixed surfactant system is decreased than the pure surfactant system [27, 28, 29].

Also, Bhattarai et al. [30, 55] studied the micellization behavior of cationic surfactant mixtures in aqueous solution as well as methyl alcohol-water mixture along with the detailed investigation of thermodynamic phenomena and very less surface properties without comparing the CMC values with theoretical models.

In order to see the synergism from theoretical models, we used the surface tension study of DTAB-rich and SDS-rich systems. In the ideal solution (components do not interact to each other) and non-ideal solution (components interact to each other) behavior for surfactants, mixture can be described by using the pseudo-phase separation model. The CMC^{id} (critical micelle concentrations of the ideal mixed system) of the catanionic systems can be assessed with the help of experimental determined CMC (critical micelle concentrations of the surfactants mixture) values of the separate surfactants using the Clint's relation [56] as in Eq. (1):

$$\frac{I}{CMC} = \frac{\alpha}{f_1^{Rub} CMC_1} + \frac{I - \alpha}{f_2^{Rub} CMC_2} \quad (1)$$

For DTAB-rich systems:

$\alpha = 0.75$ = the mole fraction of DTAB in the total mixed solute

CMC = Critical micelle concentration of mixed surfactant system for DTAB-rich

CMC_1 = Critical micelle concentration of Pure DTAB for DTAB-rich system

CMC_2 = Critical micelle concentration of Pure SDS for DTAB-rich system

f_1^{Rub} = the activity coefficient of DTAB in the mixed micelle

f_2^{Rub} = the activity coefficient of SDS in the mixed micelle.

If there is no interaction, then ($f_1^{Rub} = f_2^{Rub} = 1$), and the Clint's relation becomes [56]:

$$\frac{1}{CMC^{id}} = \frac{\alpha}{CMC_1} + \frac{1-\alpha}{CMC_2} \quad (2)$$

At 293.15 K, mixed CMC of DTAB rich = 13.00 mM [30], CMC of DTAB = 14.80 mM [57], CMC of SDS = 8.00 mM [58] then CMC^{id} becomes 12.21mM. Hence $CMC - CMC^{id} = 0.79$, the positive value indicates the antagonistic interaction.

Similarly, for SDS-rich systems:

$\alpha = 0.75$ = the mole fraction of SDS in the total mixed solute

CMC = Critical micelle concentration of mixed surfactant system for SDS-rich

CMC_1 = Critical micelle concentration of Pure SDS for SDS-rich system

CMC_2 = Critical micelle concentration of Pure DTAB for SDS-rich system

At 293.15 K, mixed CMC of SDS-rich = 6.011 mM [30], then CMC^{id} becomes 9.04 mM. Hence $CMC - CMC^{id} = -3.03$, the negative value indicates the synergistic interaction.

The experimentally obtained CMC values were seen to be less than CMC^{id} values [59, 60] showing not positive dispossession from ideality, and hence the synergistic interaction exists between the surfactants [61].

To explain more for the nonideality of the mixed micellization system, the popular model can be used as in the form of Eq. (3) where x can be obtained by solving Eq. (3) iteratively [51]:

$$x^2 \ln \left(\alpha \frac{CMC}{x CMC_1} \right) / (1-x)^2 \ln \left[\frac{(1-\alpha) CMC}{(1-x) CMC_2} \right] = 1 \quad (3)$$

Where x = the micellar mole fraction of the mixed surfactants.

On putting the value of x , β^m (the micellar interaction parameter) is obtained by the given relation,

$$\beta^m = \ln \left(\alpha \frac{CMC}{x CMC_1} \right) / (1-x)^2 \quad (4)$$

The evaluated values of β^m for SDS-rich system at 293.15 K were used in Rubingh's equations to calculate the activity coefficients (f_1^{Rub} and f_2^{Rub}) as described in the literature [51]:

$$\ln f_1^{Rub} = \beta^m (1-x)^2 \quad (5)$$

$$\ln f_2^{Rub} = \beta^m x^2 \quad (6)$$

According to the concept of Rubingh and Rosen [62, 63], we can manifest the composition of the saturated mixed monolayer in the range of 0.2–0.8 as the mole fraction of one component of the surfactants mixture in the bulk phase. So, we used the range of $x = 0.2$ to 0.8 for the calculation of f_1^{Rub} and f_2^{Rub} .

With the help of f_1^{Rub} and f_2^{Rub} , the values of the Gibbs free energy of SDS and DTAB mixing in the saturated monolayer for SDS-rich system can be calculated from the Eq. (7) as mentioned in the literature [62, 63]:

$$\Delta G^{\text{m}} = RT(x \ln f_1^{\text{Rub}} + x \ln f_2^{\text{Rub}}) \quad (7)$$

If we use $x = 0.5$ in Eq. (3), the left-hand side gives the value 1, and in such case β^{m} has -2.56742 value indicating synergistic interaction. The negative value ($-1564.36 \text{ J mol}^{-1}$) in Table 3 of Gibbs free energy of mixture also proves the synergistic interaction.

At ideal state minimum surface area ($A_{\text{ideal,in}}$) per monomer has been analyzed through Eq. (8). Let us suppose there is synergistic interaction then Eq. (8) can be written [64] as:

$$A_{\text{ideal,in}} = x A_{\text{min},1} + (1 - x) A_{\text{min},2} \quad (8)$$

Where $A_{\text{min},1}$ ($39.65 \text{ A}^2 \text{ molecule}^{-1}$) and $A_{\text{min},2}$ ($56.54 \text{ A}^2 \text{ molecule}^{-1}$) are the area occupied by SDS and DTAB molecules respectively at 293.15 K [30]. On putting the value of $x = (0.50 \text{ at } 293.15 \text{ K})$ in Eq. (8), we get A_{ideal} ($48.095 \text{ A}^2 \text{ molecule}^{-1}$).

It is observed that the value of $A_{\text{ideal,in}}$ is higher than A_{min} ($44.70 \text{ A}^2 \text{ molecule}^{-1}$) of SDS-rich system at 293.15 K [30].

Table 3. Values of $x, \beta^{\text{m}}, f_1^{\text{Rub}}, f_2^{\text{Rub}}$ and ΔG^{m} from Rubingh model of SDS-rich in aqueous medium at $T = 293.15 \text{ K}$.

S.N.	x	β^{m}	f_1^{Rub}	f_2^{Rub}	$\Delta G^{\text{m}} (\text{Jmol}^{-1})$
1.	0.8	-27.7964	0.329013	1.885×10^{-8}	-36854.3
2.	0.7	-10.8703	0.376006	0.004866	-10756.4
3.	0.6	-5.1511	0.438662	0.156599	-3917.0
4.	0.5	-2.5674	0.526377	0.526377	-1564.4
5.	0.4	-1.1631	0.657944	0.830224	-589.6
6.	0.3	-0.2674	0.877214	0.976225	-113.4
7.	0.2	0.4288	1.315724	1.017297	142.1

The lowered $A_{\min}$ value indicates a significant synergistic interaction between the components of the mixed surfactant system for SDS-rich and hence the strongest attraction between the oppositely charged head groups [65].

3.3. Relation between $A_{\min}$ and π_{cmc} m Nm⁻¹

The π_{cmc} gives the information about the lateral interaction between SDS-rich and DTAB-rich molecules whereas $A_{\min}$ describes the area per molecule provides the information on the degree of packing and orientation of the adsorbed SDS-rich and DTAB-rich molecules. Here, π_{cmc} and $A_{\min}$ increases with increasing temperature (Figs. 4 and 5). The data for π_{cmc} and $A_{\min}$ at 293.15 K for DTAB-rich and SDS-rich were taken from the literature [30] as for π_{cmc} (45.74, 47.91, 49.71 m Nm⁻¹ of DTAB-rich) and (41.95, 43.85, 44.61 m Nm⁻¹ of SDS-rich) at 293.15, 298.15 and 303.15 K respectively and for $A_{\min}$ (58.07, 59.62, 61.59 Å²molecule⁻¹ of DTAB-rich) and (44.70, 49.37, 51.82 Å²molecule⁻¹ of SDS-rich) at 293.15, 298.15 and 303.15 K respectively investigated.

As Both DTAB-rich and SDS-rich show convex nature of curves. There is a sharp increment of $A_{\min}$ and π_{cmc} with temperature in DTAB-rich system compare with SDS-rich, and the curve for DTAB-rich is higher than the curve of SDS-rich.

We also plot the curve of π_{cmc} $A_{\min}$ with π_{cmc} : the concave pattern of the curves is observed for SDS-rich and DTAB-rich systems. Such type of plot of π_{cmc} $A_{\min}$ with π_{cmc} was also observed for decosyltriethylammonium bromide at the air-water and oil-water interfaces in the presence and absence of salts [66]. But in that literature [66] it was observed that the curves of decosyltriethylammonium bromide at the air-water and oil-water interfaces in the presence of salts were lower in comparison

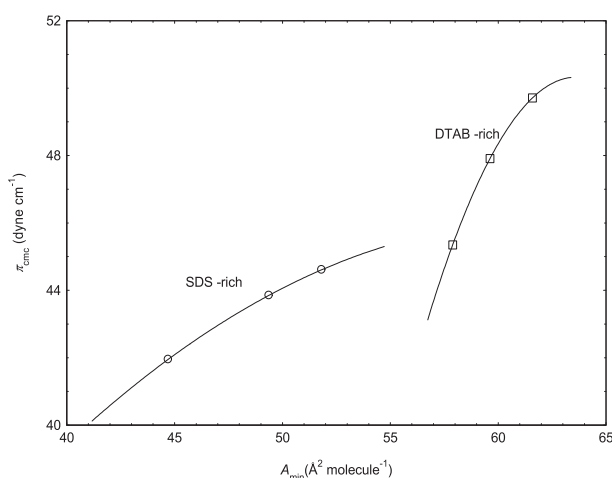


Fig. 4. Variation of π_{cmc} with $A_{\min}$: open circles (SDS-rich), open squares (DTAB-rich) at 293.15, 298.15 and 303.15 K.

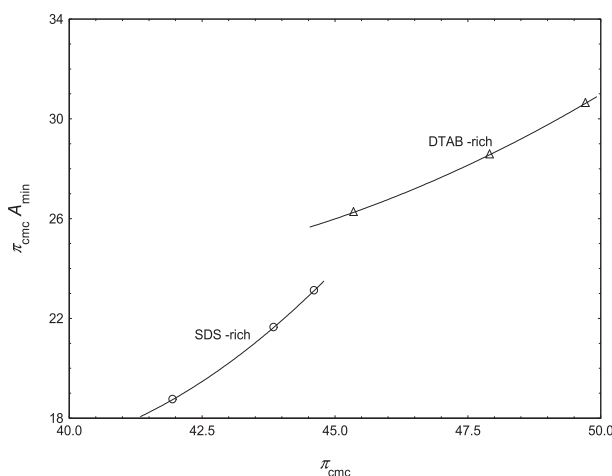


Fig. 5. Variation of $\pi_{cmc} A_{min}$ with π_{cmc} : open circles (SDS-rich), open triangles (DTAB-rich).

to the curve of decosyltriethylammonium bromide at the air-water and oil-water interfaces in the absence of salts. The pattern of the curves was almost linear for decosyltriethylammonium bromide at the air-water and oil-water interfaces. But the presence of KBr in decosyltriethylammonium bromide at the air-water produced the concave nature of curve whereas in the presence of NaCl in the oil-water interface, the curve showed the sharp linear nature with an increase of π and the curve was higher than the KBr curve. In our case, the curve for DTAB-rich is higher than the curve of SDS-rich.

The plot of area (A_{min}) against $1/\pi_{cmc}$ gives interesting results (Fig. 6). The nature of the curves is linear for both DTAB-rich and SDS-rich systems. But the DTAB-rich has the higher curve than SDS-rich curve with a slope (-19.2) , intercept

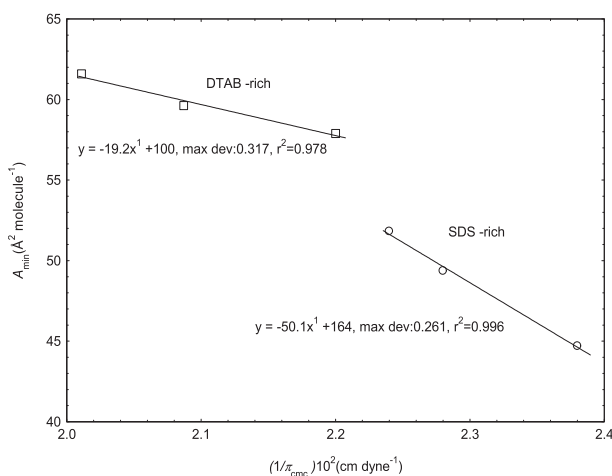


Fig. 6. Variation of A_{min} with $1/\pi_{cmc}$: Open circles (SDS-rich), open squares (DTAB-rich).

(100) and the correlation coefficient ($r^2 = 0.978$) and whereas SDS-rich has a slope (-50.1), intercept (164) and the correlation coefficient ($r^2 = 0.996$). Such linearity was also found when a plot of $1/\pi_{\text{cmc}}$ against A_{min} for the adsorption of butyric acid at the benzene-water interface [67]. The linear plots for various dibasic acids at the heptane-water interface [68] were also similar behavior with our systems.

3.4. Correlation of $\Delta G_{\text{eff}}^{\circ}$ with temperature

The difference between $\Delta G_{\text{ads}}^{\circ}$ and $\Delta G_{\text{m}}^{\circ}$ is called effective Gibb's free energy ($\Delta G_{\text{eff}}^{\circ}$), and their corresponding values are given in Table 4. $\Delta G_{\text{eff}}^{\circ}$ decreases with an increase of temperature for SDS-rich and DTAB-rich systems (Table 4 and Fig. 7).

It is also found that there is a concave curve with an increase of temperature for SDS-rich whereas, in DTAB-rich, the curve became linear with a correlation coefficient ($r^2 = 1$) with an increase of temperature. The data for $\Delta G_{\text{ads}}^{\circ}$ and $\Delta G_{\text{min}}^{\circ}$ at 293.15 K for DTAB-rich and SDS-rich were taken from the literature [30]. As for $\Delta G_{\text{ads}}^{\circ}$ (-49.9 , -51.1 , -52.5 kJ mol^{-1} of DTAB-rich) and (-43.32 , -45.29 , -46.31 kJ mol^{-1} of SDS-rich) at 293.15, 298.15 and 303.15 K respectively and for $\Delta G_{\text{min}}^{\circ}$ (-33.67 , -33.88 , -34.03 kJ mol^{-1} of DTAB-rich) and (-31.87 , -32.25 , -32.38 kJ mol^{-1} of SDS-rich) at 293.15, 298.15 and 303.15 K respectively investigated. Our finding of $\Delta G_{\text{eff}}^{\circ}$ variation with temperature is similar to the variation of $\Delta G_{\text{ads}}^{\circ}$ and $\Delta G_{\text{min}}^{\circ}$ with temperature (Fig. 7).

Table 4. Values of efficiency of adsorption (pC_{20}), Aggregation number (N), $\Gamma/\Gamma_{\text{max}}$, Effective Gibbs free energy ($\Delta G_{\text{eff}}^{\circ}$) and $\frac{CMC}{C_{20}}$ of SDS-rich and DTAB-rich in aqueous medium at $T = 293.15$, 298.15 and 303.15 K.

Temperature (K)	pC_{20}	Aggregation Number (N)	$\Gamma/\Gamma_{\text{max}}$	$\Delta G_{\text{eff}}^{\circ} (\text{kJ mol}^{-1})$	$\frac{CMC}{C_{20}}$
SDS-rich					
293.15	2.22	78	0.990328	-11.29	3.370736
298.15	2.20	71	0.992649	-13.04	3.810795
303.15	2.17	67	0.996035	-13.93	4.606244
DTAB-rich					
293.15	1.87	60	0.998469	-15.83	6.135483
298.15	1.85	59	0.999018	-17.22	7.539090
303.15	1.83	56	0.999327	-18.47	8.894329

Errors limits of pC_{20} , N , $\Gamma/\Gamma_{\text{max}}$, $\Delta G_{\text{eff}}^{\circ}$ and $\frac{CMC}{C_{20}}$ are within $\pm 5\%$, $\pm 7\%$, $\pm 6\%$, $\pm 4\%$ and $\pm 5\%$ respectively.

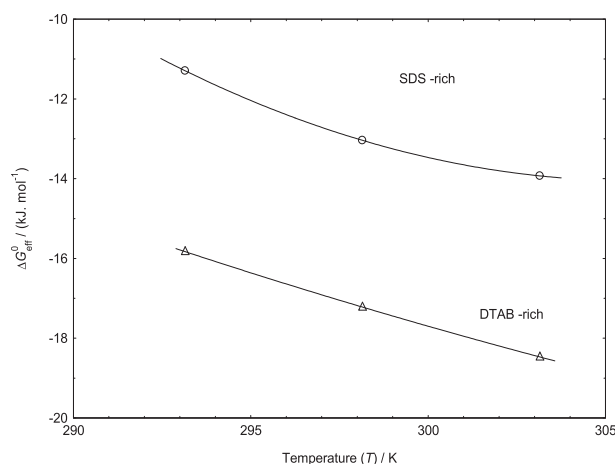


Fig. 7. Variation of $\Delta G_{\text{eff}}^{\circ}$ with temperature.

3.5. Correlation of N with temperature

An aggregation number (N) is a description of the number of molecules present in a micelle once the CMC is reached [8]. 55 and 64 were the aggregation numbers for DTAB and SDS in water at 25 °C in the literature [69]. 36 was the aggregation number of DTAB at 45 °C [70], and 59 was the aggregation number of SDS at 41.5 °C [71]. Thus, the increase in temperature decreases the aggregation numbers of the surfactant molecule.

Here we have determined the aggregation numbers by the simple equation with varying A_m described elsewhere [72].

$$N = \frac{4\pi l_c^2}{A_m} \quad (9)$$

Where A_m is the area occupied by per surfactant molecule and l_c (hydrophobic tail length).

59 and 71 are our calculated aggregation numbers for DTAB-rich and SDS-rich respectively at 298.15 K (Table 4). It means that higher values of aggregation numbers for both DTAB-rich and SDS-rich system in comparison with individual DTAB and SDS.

The reason for higher N in mixed systems is that the optimum mixed micelles of DTAB and SDS for SDS-rich and DTAB-rich has lower polarity in comparison with single micelles. That makes the compression of a diffuse electric double layer of the mixed micelles and hence the reduction of the rejection interaction between two kinds of the ion head groups [73].

In our case SDS-rich and DTAB-rich systems, N decreases with increasing temperature [71]. DTAB-rich shows a linear decrease of N upon increasing T whereas for

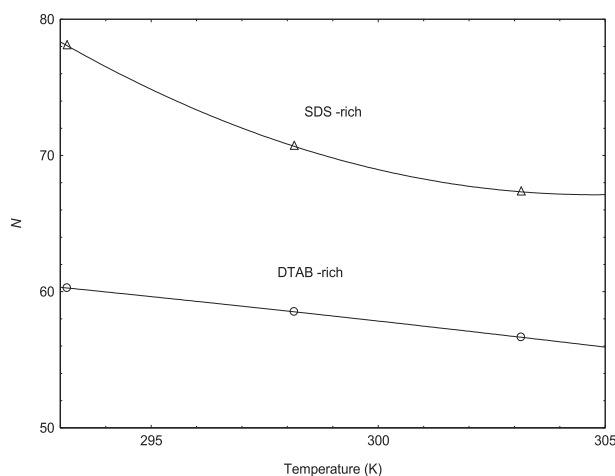


Fig. 8. Variation of N with temperature.

SDS-rich shows the concave nature of decrease variation of N with an increase of temperature (Fig. 8). The reason for N decreases with increasing temperature may be the dissociation of the intra-micellar excimers play the role for the complete interpretation of the results at high temperature [71].

3.6. Correlation of pC_{20} with temperature

The negative logarithm of the concentration of surfactant in the bulk phase necessary to make a 20 dyn/cm reduction in the surface tension of the solvent is the efficiency of adsorption (pC_{20}).

The minimum concentration of surfactant can be obtained when we plot γ versus $\log C$. The bulk liquid phase concentration of surfactant required to depress the surface tension of the solvent by 20 dyn/cm is a good measure of the efficiency of adsorption of the surfactant.

We have the relation of pC_{20} for the mixed surfactants system [74] as:

$$pC_{20} = \frac{\pi_{cmc} - 20}{2.303nRT \Gamma_{\max}} - \log cmc \quad (10)$$

Here, the maximum surface excess concentration ($\Gamma_{\max}$) is calculated by the relation of ($A_{\min} = 1/N_A \Gamma_{\max}$) where N_A stands for Avogadro's number, $n = 2$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, T = Temperature, surface pressure (π_{cmc}), cmc = critical micelle concentration and the values of cmc s were taken from the literature at 293.15 K [30] and for rest temperatures, we have calculated as 0.0063 and 0.0067 mol. L^{-1} for SDS-rich at 298.15 and 303.15 K respectively and for DTAB-rich as 0.01401 and 0.01470 mol. L^{-1} at 298.15 and 303.15 K respectively. On putting these values in Eq. (10), we get pC_{20} for DTAB-rich and SDS-rich systems in Table 4.

2.97 [75] and 2.72 [76] were the pC_{20} values for DTAB and SDS in water at 298.15 K. 1.85 and 2.20 are our calculated pC_{20} for DTAB-rich and SDS-rich respectively at 298.15 K (Table 4). For DTAB-rich and SDS-rich, pC_{20} values decrease in comparison with pure DTAB and SDS indicating more and more surface adsorption [77].

It is observed that the pC_{20} values for DTAB-rich and SDS-rich decreases with the increase of temperature (Table 4 and Fig. 9). This suggests that elevated temperature is not favorable for micellization, corresponding to the CMC trends [76]. The variation of pC_{20} with temperature in DTAB rich is linear whereas SDS-rich slightly convex nature of the curve (Fig. 9).

3.7. Correlation of $\frac{CMC}{C_{20}}$ with temperature

C_{20} is the concentration of surfactant in the bulk phase that produces a reduction of 20 dyne/cm in the surface tension of the solvent. There is a decrease or an increase of $\frac{CMC}{C_{20}}$. A decrease of $\frac{CMC}{C_{20}}$ indicates that the micellization facilitated more than adsorption whereas an increase of $\frac{CMC}{C_{20}}$ indicates that the adsorption facilitated more than micellization. Therefore, the ratio $\frac{CMC}{C_{20}}$ provides information about the adsorption and micellization processes.

In our system, the increase of $\frac{CMC}{C_{20}}$ with temperature indicates that the adsorption facilitated more than micellization (Fig. 10). Generally, ionic surfactants with a single straight chain hydrophobic group in aqueous system show low $\frac{CMC}{C_{20}}$ ratios of 3 or less [51]. We have also observed the value of $\frac{CMC}{C_{20}}$ more than 3 and less than 9 for DTAB-rich and SDS-rich systems in our studied temperatures range (293.15–303.15 K).

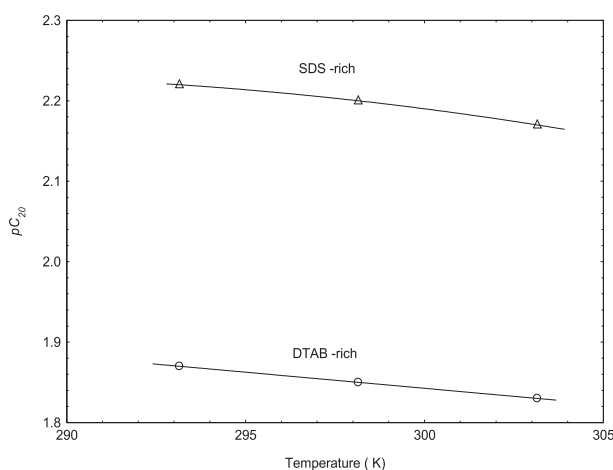


Fig. 9. Variation of pC_{20} with temperature.

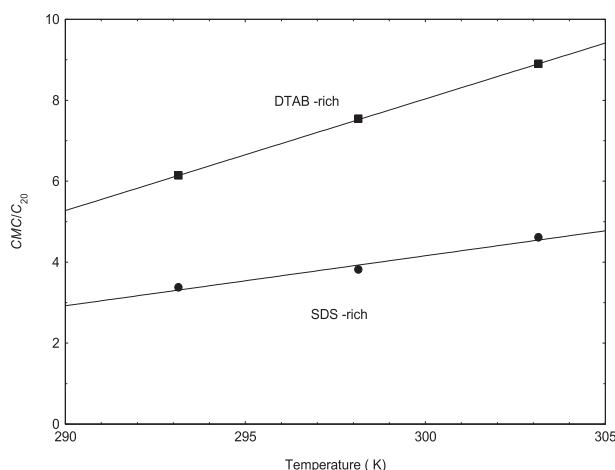


Fig.10. Variation of CMC/C_{20} versus temperature.

When the surface is essentially saturated then the surface tension of the solvent has been reduced by 20 dynes/cm which is generally the case for most surfactants, then for the linear portion of the plot, the Gibbs adsorption equation becomes (11) [51] as:

$$\pi_{\text{cmc}} \approx 20 + 2.3nRT\Gamma_{\text{max}} \log\left(\frac{CMC}{C_{20}}\right) \quad (11)$$

This equation shows that Γ_{max} and $\frac{CMC}{C_{20}}$ are in parallel fashion. It means if one increases then other also increases or if one decreases then other also decreases. By doing so, the reduction of effectiveness of surface tension exists. Sometimes we can see the large values of ratio $\frac{CMC}{C_{20}}$ which may be due to steric barriers associated with the packing of these bulky chains into the micelle. One can observe that the value of C_{20} plays a vital role in the increment or decrement of $\frac{CMC}{C_{20}}$. If the value of C_{20} is increased more than the CMC , then $\frac{CMC}{C_{20}}$ value is decreased or vice-versa. Also, from the above discussion, $\frac{CMC}{C_{20}}$ is a measure of the tendency to form micelles relative to the tendency to adsorb at the air/water interface [77, 78]. The values of $\frac{CMC}{C_{20}}$ for DTAB-rich and SDS-rich at 293.15, 298.15 and 303.15 K are given in Table 4.

3.8. Correlation of $\Gamma/\Gamma_{\text{max}}$ with temperature

On increasing temperature, the value of $\Gamma/\Gamma_{\text{max}}$ increases for both DTAB-rich and SDS-rich systems. But for DTAB-rich systems, there is a monotonous increase of the value of $\Gamma/\Gamma_{\text{max}}$ with temperature within the range of 0.998 to less than 1 whereas for SDS-rich systems; there is sharply increase of the value of $\Gamma/\Gamma_{\text{max}}$ with temperature within the range of 0.990 to less than 0.998. Moreover, DTAB-rich system has a linear variation for $\Gamma/\Gamma_{\text{max}}$ with an increase of temperature

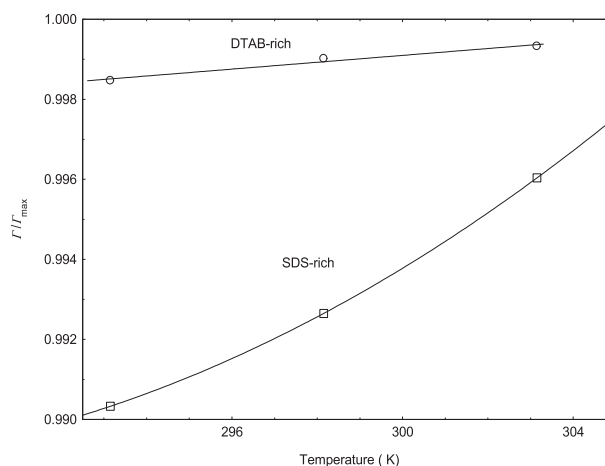


Fig. 11. Variation of $\Gamma/\Gamma_{\max}$ versus temperature.

whereas SDS-rich system has a concave curve for $\Gamma/\Gamma_{\max}$ with an increase of temperature (Fig. 11).

Applying the Frumkin isotherm equation provided in the literature [51], it confirmed that the concentration value at which γ of water is diminished by 20 mN/m, the ratio of the Gibbs surface excess concentration (Γ) to the maximal ($\Gamma_{\max}$) one is detected in between 0.84 and 0.999.

We have calculated the $\Gamma/\Gamma_{\max}$ values for DTAB-rich and SDS-rich systems from the equation used in the literature [51]:

$$\pi_{\text{cmc}} = -RT\Gamma_{\max} \ln \left(1 - \Gamma/\Gamma_{\max} \right) \quad (12)$$

Our values of $\Gamma/\Gamma_{\max}$ for DTAB-rich and SDS-rich systems perfectly matched within range of the literature [51, 79].

3.9. Interaction between dyes and mixed surfactants

In aqueous solutions, MO exhibits two maximum absorption bands at 275 nm and 465 nm [80] whereas MB also exhibits two maximum absorption bands at 245 nm and 295 nm at 298.15 K [81]

The equal amount of MO and MB as $2.5 \times 10^{-5} \text{ mol L}^{-1}$ were taken as dyes to see the interaction with mixed surfactants in similar manners. Both dyes interact with SDS-rich systems produced cloudy in the preparation of solutions whereas clear and homogenous solutions were observed in 1 ml of MO with 2ml each solution (0.003264, 0.002976, 0.001536 and 0.000864 mol L^{-1} DTAB-rich systems) at Fig. 12 [20] and in 1 ml of MB with 2ml each solution (0.003264, 0.002976,

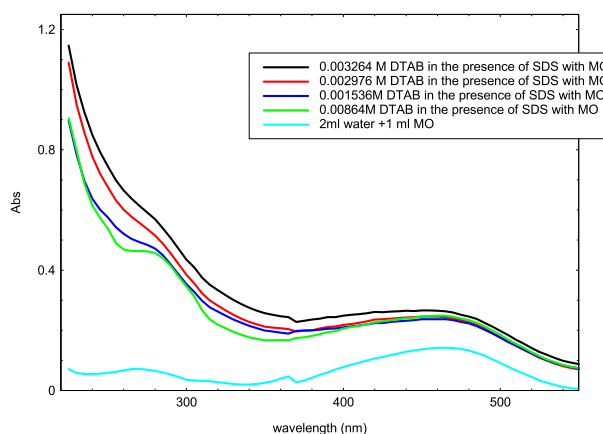


Fig. 12. Absorption spectra of DTAB-rich surfactant in the presence of MO. Copyright permission from Royal Society Open Science 6(2019)181979.

0.002496, 0.002016, 0.001536 and 0.000864 mol L⁻¹ DTAB-rich systems) at Fig. 13 [20]. So, the maximum absorption values for MO and MB at 465nm (0.142) and 295nm (0.584) are taken for evaluation of binding constants when interacting with mixed surfactants as they have sharp peaks with or without the presence of mixed surfactants. There were no blue or red shifts for the entire DTAB-rich with MO and DTAB-rich with MB systems, but the only hyperchromic shift was noticed within the investigated concentration ranges (Figs. 12 and 13) [20]. So, we are interested to see the binding effects and standard free energy change.

For determination of Binding Constants of MO and MB with DTAB-rich systems, one needs to describe as:

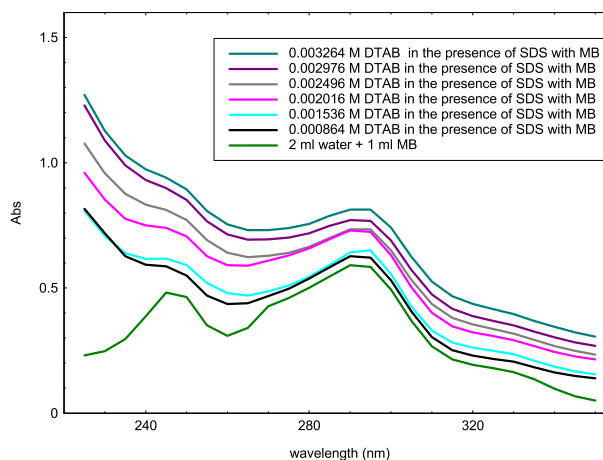
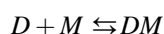


Fig. 13. Absorption spectra of DTAB-rich surfactant in the presence of MB. Copyright permission from Royal Society Open Science 6(2019)181979.

Where D , M , DM , and K_b represent the dye, micelle, dye-micelle association and binding constant respectively. The binding constant, K_b , and molar extinction coefficient, ϵ_m can be determined using the Benesi–Hildebrand equation in the following modified form as in Eq. (13) by us without using CMC values of mixed surfactants with dyes. Without CMC used for the calculation of binding constant by taking surfactant concentration was also reported on UV studies of MB with Triton X-100 in reverse micelle media in the literature [82]. But normally in the literature, CMC of surfactant and dye interaction was taken for calculation of binding constant [83,84]:

$$\frac{D_T}{\Delta A} = \frac{1}{(\epsilon_m - \epsilon_o)} + \frac{1}{K_b(\epsilon_m - \epsilon_o)C_s} \quad (13)$$

The molar extinction coefficient of MO (ϵ_o) at 465nm was calculated as 5680 (± 0.01) at 298.15 K (± 0.1), and the molar extinction coefficient of MB (ϵ_o) at 295nm was calculated as 23360 (± 0.01) at 298.15 K (± 0.1).

Where D_T is the concentration of dye, $\Delta A = A - A_o$ is the difference between the absorbance of dye in the presence and absence of DTAB-rich, ϵ_m is the molar extinction coefficient of dye fully bound to micelles, ϵ_o is the molar extinction coefficient of the dye, K_b is the binding constant, C_s is the concentration of DTAB-rich systems.

When we plot the graph between $\frac{D_T}{\Delta A}$ and $\frac{1}{C_s}$ for DTAB-rich with MO interaction as in Fig. 14. The linear relationship having correlation coefficients ($r^2 = 1$) indicates that the validity of Lambert-Beer law. From the slope (6.59×10^{-8}) and the intercept (1.88×10^{-4}), the binding constant (K_b) was found to be 2852.80. Similarly, when we plot the graph between $\frac{D_T}{\Delta A}$ and $\frac{1}{C_s}$ for DTAB-rich with MB interaction as in Fig. 15. The linear relationship having correlation coefficients ($r^2 = 1$) indicates that the validity of Lambert-Beer law. From the slope ($5.63 \times$

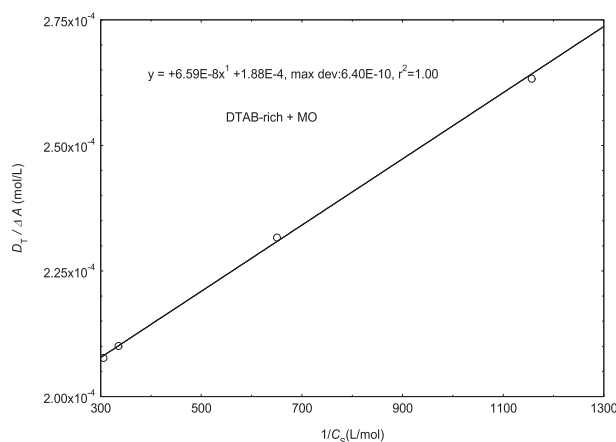


Fig. 14. The plot $\frac{D_T}{\Delta A}$ against $\frac{1}{C_s}$ for DTAB-rich-MO systems.

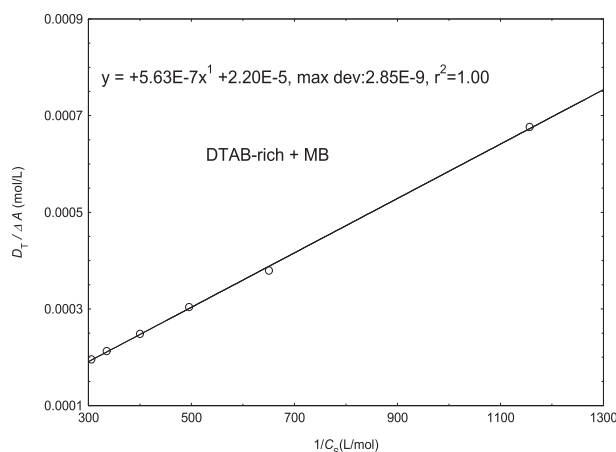


Fig. 15. The plot $\frac{D_r}{\Delta A}$ against $\frac{1}{C_s}$ for DTAB-rich-MB systems.

10^{-7}) and the intercept (2.20×10^{-5}), the binding constant (K_b) was found to be 39.07. The value of binding constant between MO and DTAB-rich systems is so high as compared to MB with DTAB-rich solution (Table 3). To verify our modified equation for evaluation of binding constants, we take the equation used by Hashemi and Sun [85]:

$$\frac{1}{\Delta A} = \frac{\epsilon_o}{\epsilon_m \times A_o} + \frac{\epsilon_o}{A_o \times K_b \times \epsilon_m \times C_s} \quad (14)$$

The symbols used in Eq. (14) has the same meanings used as in Eq. (13).

When we plot the graph $\frac{1}{\Delta A}$ versus $\frac{1}{C_s}$ for DTAB-rich with MO interaction as in Fig. 16. The linear relationship having correlation coefficients ($r^2 = 1$) indicates that the validity of Lambert-Beer law. From the slope (0.00261) and the intercept (7.53), the binding constant (K_b) was found to be 2885.06.

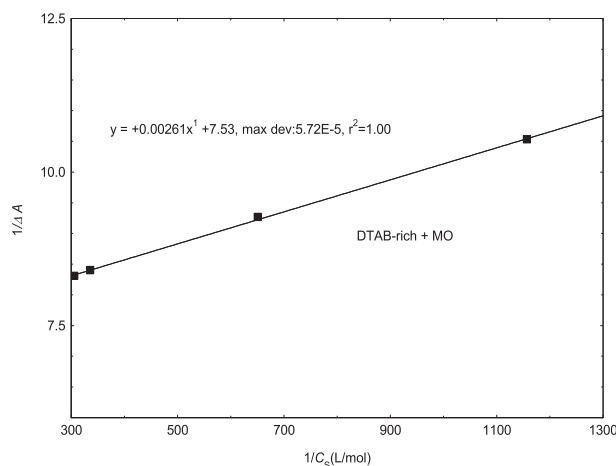


Fig. 16. The plot $1/\Delta A$ against $1/C_s$ for DTAB-rich-MO systems.

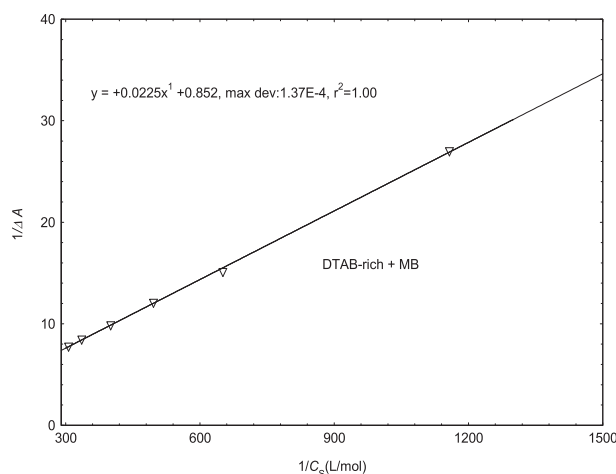


Fig. 17. The plot $1/\Delta A$ against $1/C_s$ for DTAB-rich-MB systems.

Similarly, when we plot the graph $\frac{D_r}{\Delta A}$ versus $\frac{1}{C_s}$ for DTAB-rich with MB interaction as in Fig. 17. The linear relationship having correlation coefficients ($r^2 = 1$) indicates that the validity of Lambert-Beer law. From the slope (0.0225) and the intercept (0.852), the binding constant (K_b) was found to be 37.87.

The binding constants calculated from Eq. (14) are closer with the binding constants determined by Eq. (13).

The thermodynamic parameter (G°) which is an indicator of the tendency of binding of MO to DTAB-rich and MB to DTAB-rich micelles, was calculated using the following equation used in the literature [86]

$$G^\circ = -RT \ln K_b \quad (15)$$

Where, R is the universal gas constant and T is the temperature of 298.15 K.

The values of G° of DTAB-rich with MB and DTAB-rich with MO are found to be -9.085 and $-19.72 \text{ kJ mol}^{-1}$ respectively from K_b calculated from Eq. (13). Similarly, the values of G° of DTAB-rich with MB and DTAB-rich with MO are found to be -9.008 and $-19.74 \text{ kJ mol}^{-1}$ respectively from K_b calculated from Eq. (14). The standard free energy change for MO with DTAB-rich systems and MB with DTAB-rich systems from our modified equation matched with the standard free energy change for MO with DTAB-rich systems and MB with DTAB-rich systems calculated from Hashemi and Sun [85] equation. The binding constants and standard free energy changes from both calculations are given in Table 5. Hence, MO interacts with DTAB-rich more easily and strongly than MB interacts with DTAB-rich at the same conditions.

To see more depth for the dyes interaction with mixed surfactants, we plot the absorbance versus $\log [C_s]$ in Fig. 18. The absorbance increases in the increase of the

Table 5. Values of absorbance of Dye in presence of DTAB-rich systems (A), absorbance of Dye in absence of DTAB-systems (A_o), concentration of DTAB-rich systems (C_s) values of binding constants (K_b), standard free energy change (G°).

A	A_o	$C_s(\text{mol} \cdot \text{L}^{-1})$	K_b	$G^\circ(\text{kJ mol}^{-1})$	$\lambda_{\text{max}}(\text{nm})$
MB with DTAB-rich					
0.712	0.584	0.003264	39.07 ^a	−9.085 ^a	295
0.702	0.584	0.002976			295
0.685	0.584	0.002496	37.87 ^b	−9.008 ^b	295
0.667	0.584	0.002016			295
0.650	0.584	0.001536			295
0.621	0.584	0.000864			295
MO with DTAB-rich					
0.263	0.142	0.003264	2852.80 ^a	−19.72 ^a	465
0.261	0.142	0.002976			
0.250	0.142	0.001536	2885.06 ^b	−19.74 ^b	465
0.237	0.142	0.000864			465

Errors limits of A , A_o , C_s , K_b , G° and λ_{max} are within ± 0.01 , ± 0.01 , ± 0.02 , ± 0.03 , ± 0.03 and ± 0.01 respectively.

^aCalculated binding constant (K_b) and standard free energy change (G°) from our modified equation.

^bCalculated binding constant (K_b) and standard free energy change (G°) from the equation [85].

concentration of DTAB-rich systems for both DTAB-rich with MB and MO. But the concave variation of the graph is noticed for DTAB-rich with MB having higher values of absorbance whereas almost linear of the graph is noticed for DTAB-rich with MO having lower values of absorbance. Polynomial equations did the fitting of the curve with correlation coefficients for both systems, $r^2 = 1$ (Fig. 18). Having higher binding constant for DTAB-rich with MO, MO with DTAB-rich looks most

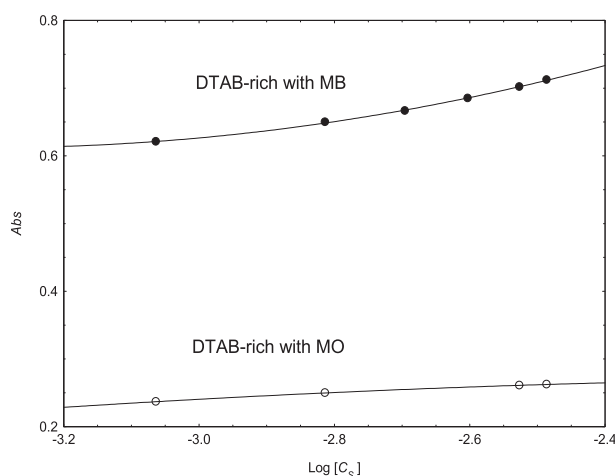


Fig. 18. Effect of DTAB-rich systems concentration on the absorbance of MB and MO.

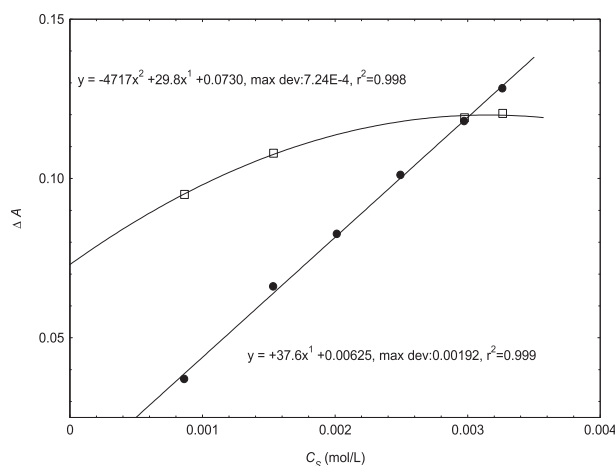


Fig. 19. ΔA (difference between the absorbance of dye in the presence and absence of DTAB-rich) versus concentration of DTAB-rich.

stable as stronger interaction. The combination between MO and DTAB-rich is probably formed at the minimum absorbances while having a lower binding constant for DTAB-rich with MB, MB with DTAB-rich looks less stable as weaker interaction. The combination of MB and DTAB-rich is probably formed at higher absorbance values. Such studies were also observed in the literature [85].

We are also interested to see the plot of ΔA (difference between the absorbance of dye in the presence and absence of DTAB-rich) with $[C_s]$ in Fig. 19. ΔA increases with the increase of the concentration of DTAB-rich systems for both DTAB-rich with MO and MB. But the convex variation of the graph is noticed for DTAB-rich with MO having higher values of ΔA by polynomial fitting with correlation coefficients, $r^2 = 0.998$ whereas linear of the graph is noticed for DTAB-rich with MB having lower values of ΔA by linear fitting with correlation coefficients, $r^2 = 0.999$ (Fig. 19).

From Fig. 19, it is seen that the increase of the concentration of DTAB-rich resulted in a gradual increase in ΔA . The highest value of ΔA is reached at $0.003264 \text{ mol L}^{-1}$ which indicates that the powerful dye-surfactant combination was produced at this concentration. By further increasing the concentration, ΔA achieved a constant value because, at higher concentrations, all the molecules of dyes are completely solubilized. The binding constant of MO with DTAB-rich seems higher than MB with DTAB-rich systems. Accordingly, G^o is higher in DTAB-rich-MB system in comparison with DTAB-rich-MO system. High Binding constant means MO may introduce stronger interactions with DTAB-rich systems. Binding constant values decreased for MB with DTAB-rich systems indicate that the hydrophobic interactions may restrict with the stable interactions of molecules. Such studies were also observed in the literature [86].

4. Conclusions

The surface tension study for mixed surfactants not only provides the detailed surface properties and thermodynamics of DTAB and SDS mixed surfactants but also indicates the antagonistic interaction for DTAB-rich system and synergetic interaction for SDS-rich system. We have observed that there is an interconnection among derived parameters from the primary surface tension data. The relation between $A_{\min}$ and π_{cmc} provides new dimensions to the scholars for SDS-rich and DTAB-rich systems. The temperature variation with the efficiency of adsorption ($\text{p}C_{20}$), Aggregation number (N), $I/\Gamma_{\max}$, Effective Gibbs free energy ($\Delta G_{\text{eff}}^{\circ}$) and $\frac{\text{CMC}}{C_{20}}$ of SDS-rich and DTAB-rich in the aqueous medium will enhance the surface properties of mixed systems especially cationic and anionic of the same charges.

The binding constants and standard free energy change calculation from our modified equation and comparison has been done by calculating the binding constants, and standard free energy change from another equation provided in the literature supports UV-vis studies on this field. The CMC calculation of tetravalent combination as (DTAB-SDS-MO or MB-H₂O) really a tough job to get accuracy from the low cost equipment. So, our concept without using CMC of such complicated systems will make it easy to calculate the binding constants and standard free energy change.

The variation of DTAB-rich systems concentration on the absorbance of MB and MO as well as the variation of the difference between the absorbance of MB and MO in the presence and absence of DTAB-rich systems with a concentration of DTAB-rich systems indicates the weak interaction for MB with DTAB-rich systems as compared to MO with DTAB-rich systems.

Declarations

Author contribution statement

Ajaya Bhattarai & Man Singh: Conceived and designed the experiments; Wrote the paper.

K. M. Sachin & Sameer Karpe: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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