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Measurements and Modelling of the Micellization of Alkyl Benzyl Dimethyl Ammonium Chloride and Cetyl Trimethyl Ammonium Chloride in Various Aqueous Media at 298.15 °K

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Abstract

The critical micelle concentration (CMC) of two cationic surfactants "alkyl benzyl dimethyl ammonium chloride (BAC), and cetyl trimethyl ammonium chloride (CTAC)" in aqueous solution of different salts, cationic dye and cationic surfactant was measured experimentally at room temperatures (298.15 °K). Four methods; conductivity, refractive index, surface tension and UV spectroscopy has been used to determine the CMC values. The CMC was found to decrease as the concentration of salts increased. Also, it was found that CMC of (BAC) and (CTAC) increase in the order: pure water > 0.001 M > 0.01 M > 0.1 M. While it increases when the methylene blue (MB) is added to the aqueous solution. The thermodynamic parameters (ΔG°_{mic}, α and β) of the micellization processes indicated that the micellization process is going spontaneous in all cases. Different surface properties of the two cationic surfactants including excess surface concentration and minimum area per molecule were also calculated using the surface tension measurements. The Davies equation was applied to calculate the Hydrophilic-Lipophilic Balance (HLB) values of the two cationic surfactants (BAC) and (CTAC) theoretically. An important parameter (Setschenow constant) was used to describe the effect of adding salt on the micelle size and shape of surfactant in its solution. The results indicate that the order of the salt effect is inversely proportional to the order of CMC values in different salts.

Keywords: Conductivity; Surface tension; Refractive index; UV spectroscopy; Micellization; modelling

1. Introduction

The surfactant word is an abbreviation of the term surface active agents, which have a binary characteristic of hydrophilicity (polar head) and hydrophobicity (nonpolar tail). The surfactants can be classified into four main group: anionic, cationic, amphoteric and non-ionic. Wide spread from the applications and uses of surfactants in most chemical industries like; detergents, paints, plastics, personal care and cosmetics, agrochemicals, pharmaceuticals, food processing and so on. recently, they play an important role in wastewater treatment. An important property of the surfactants is the critical micelle concentration (CMC), its defined as the value at which the solution property of the molecule shows an abrupt change. Depending on the changes in physical properties CMC value can be measured, such as electrical conductivity, turbidity, surface tension,

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interfacial tension, solubilization and auto diffusion [1].

Many authors studied the effect of salts in the CMC value of the surfactants, depending on size and nature of counter-ions, micellar morphology can be controlled by addition of salts.

In the presence of fixed concentrations of NaCl and Na_2SO_4, interactions between the polyvinyl pyrrolidone (PVP) polymer and the cetylpyridinium chloride (CPC) surfactant are investigated using the conductivity measuring technique [2]. Conductometric and steady-state fluorescence methods, as well as varying the co-solvent composition, were used to investigate the micellization properties of cetyl trimethyl ammonium bromide (CTAB) in acetonitrile/water mixtures [3]. The conductivity technique was employed to study the interactions between PVP polymer and two cationic surfactants (CTAC and CTAB). The interactions are found to be integrally supportive [4]. Using the conductivity measurement technique, the critical micelle concentration of sodium dodecyl sulphate (SDS) and cetyl trimethyl ammonium bromide in divalent and trivalent sodium salts solution (Na_2CO_3 and Na_3PO_4) was calculated [5]. Because of its academics and industrial applications, [6] studied the thermodynamic parameters of sodium n-dodecanoyl sarcosinate in different aqueous solution from divalent salts ($MgCl_2$ and Na_2SO_4). On the other hand, [7] observed the effect of adding KCl, Na_2CO_3, C_2H_5COONa and CH_3COONa to critical micelle concentration of mixed surfactants system (cationic-non-ionic).

In addition to that, Many authors have been studied the micellization behaviour of cetyltrimethylammonium bromide in presence and absence of Na_2SO_4, $MgSO_4$, NaCl and KCl in aqueous and methanol-water mixed solvent media at different room temperatures [8–11].

Dye-Surfactant associations are important in dyeing process, dye separation processes such as cloud point extraction or micellar enhanced ultrafiltration. Many quantitative and qualitative techniques (potentiometry, conductometry, or ion selective electrodes) were used for description the dye–surfactant interactions [12–15].

William Griffin, in the late 1940s, introduced the Hydrophilic-Lipophilic Balance system (HLB) as a way of figuring out which emulsifier would work best with the oil phase of an emulsified product. All emulsifiers have a hydrophilic head that is generally composed of a water-soluble functional group and a lipophilic tail generally composed of a fatty acid or fatty alcohol [16].

The HLB values of most non-ionic surfactants can be calculated from the theoretical composition. For most polyhydric alcohol esters of fatty acids, approximate HLB values can also be calculated from the saponification number [17]. Recently gas chromatographic, titration and surface tension methods [18] have also been published. Yet, among all those methods, Davies' method has been most widely used [16].

An important parameter (Setschenow constant) was used to describe the effect of adding salt on the micelle size and shape of surfactant in its solution [19–21].

The present work aims to study the effect of different salts and cationic dye in the micellization of Alkyl Benzyl Dimethyl Ammonium Chloride (BAC), and Cetyl Trimethyl Ammonium (CTAC) surfactants in aqueous solutions at 298.15 ^{0}K using different measurements such as; conductivity, refractive index, surface tension and UV spectroscopy. Also, to study the addition effect of the two surfactants to each other before and after their CMC values.

## 2. Experimental

2.1. Materials

The Reg. CAS number, the supplier, the purity, and the purification methods for the two surfactants (Structure **1** and **2**), salts and cationic dye are presented in **Table 1**. All solutions were prepared in a cleaned glass volumetric flask as reported in previous research [22]. Stock solutions with a concentration (0.1 mol L^{-1}) and (0.01 mol L^{-1}) from the BAC and CTAC surfactants, respectively, were prepared using bidistilled water with conductivity less than 2 μScm^{-1}.

The remaining % of the BAC (50%) and CTAC (70%) concentration is water and was taken into account in the preparation of the stock solution. Also Stock aqueous solutions with three concentrations (0.001, 0.01 and 0.1 mol. L^{-1}) were prepared for all the salts.

Beside to that, a fixed concentration ($3x10^{-5}$ mol L^{-1}) from methylene blue (MB) were prepared.

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Table 1. CAS reg. no., the supplier, the purity, and the purification methods of the materials.

Component	CAS reg. no.	Supplier	Purity %	purification method
BAC	68424-85-1	CISMA, Italy	50.0	used as received
CTAC	112-02-7	CISMA, Italy	30.0	used as received
Sodium Iodide	7681-82-5	Oxford	99.5	used as received
Sodium Chloride	7647-14-5	LABCO chemical LTD	99.5	used as received
Sodium Bromide	7647-15-6	LABCO chemical LTD	99.0	used as received
Sodium Phosphate	7601-54-9	Sigma-Aldrich	96.0	used as received
Sodium Benzoate	532-32-1	EL-Nasr pharmaceutical Co.	99.0	used as received
Potassium Chloride	7447-40-7	Alpha chemicals	99.5	used as received
Potassium Bromide	7758-02-3	LABCO chemical LTD	99.0	used as received
Potassium Carbonate	584-08-7	LABCO chemical LTD	99.9	used as received
Magnesium Sulphate	7487-88-9	Sigma-Aldrich	99.5	used as received
Zinc Sulphate	7446-20-0	Sigma-Aldrich	99.0	used as received
Methylene Blue	122965-43-9	Sigma-Aldrich	$\geq 82.0\ \%$	used as received
Bidistilled Water	7732-18-5	Our lab	$\kappa < 2.0\ \mu S\ cm^{-1}$	distillation
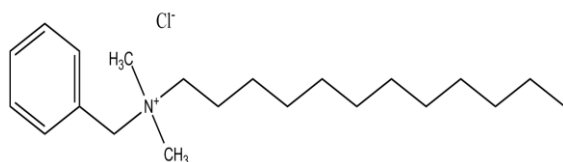
Structure 1. *Alkyl Benzyl Dimethyl Ammonium Chloride (BAC)*

$$C_6H_5CH_2N(CH_3)_2C_{12}H_{25}Cl$$
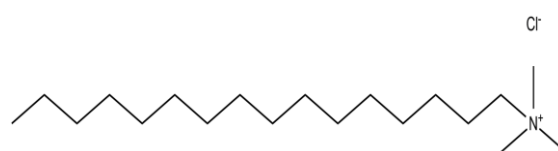
Structure 2. *Cetyl Trimethyl Ammonium Chloride (CTAC)*

$$CH_3(CH_2)_{15}N(Cl)(CH_3)_3$$
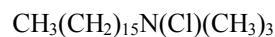
2.1. Methods

2.1.1. Conductivity measurement

The conductivity measurements were carried as reported in previous research [22].

2.1.2. Refractive index and surface tension measurement

The refractive index measurements and surface tension was carried out using Abbe refractometer (Krüss BRIX RI DR101-60) and a digital tensiometer K9 (Krüss, Germany - ring method) respectively. The refractive index and surface tension of the two surfactants in salts, cationic dye and surfactant aqueous solutions was measured as a function of concentration at 298.15 $^\circ$K. A different solutions concentration from surfactants were prepared started with 0.0001 to 0.02 mol/L. Bidistilled water sample firstly was measured to make a calibration for the apparatus at the same temperatures, then started the measurements with the diluted concentration, in each measurement an average for three reading was taken to avoid errors and finally it used for calculations and discussion.

2.1.3. UV Spectrophotometer measurement

The ultra-violet measurements were carried out using HACH DR6000™ UV VIS Spectrophotometer. The UV absorbance of the two surfactants in dye aqueous solutions was measured as a function of concentration at 298.15 $^\circ$K. A different concentration from surfactants solutions (0.0001 to 0.02 mol/L) were prepared in fixed concentration of dye aqueous solution (3 x10^{-5} mol L^{-1}).

Finally, the temperature of the solution for all the previous measurements was kept constant within ± 0.1 $^\circ$K of a desired temperature (298.15 $^\circ$K) using an ultrathermostat of type (MLW 3230, Germany).

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3. Results and discussion

3.1. CMC determination

The conductivity of the (salt + surfactant), (cationic dye + surfactant) and (surfactant + surfactant) mixed systems in aqueous solvent has been measured experimentally at room temperature (298.15 ^{0}K) as described in the experimental section.

To estimate the CMC of the two surfactants in the previous mixed solution at room temperature, the relation between conductivity and concentration of the surfactants was done as presented in **Figures 1 and 2 as an example**. There CMC values has been measured experimentally at room temperature (298.15 $^°$K) were collected in **Tables 2-4.**
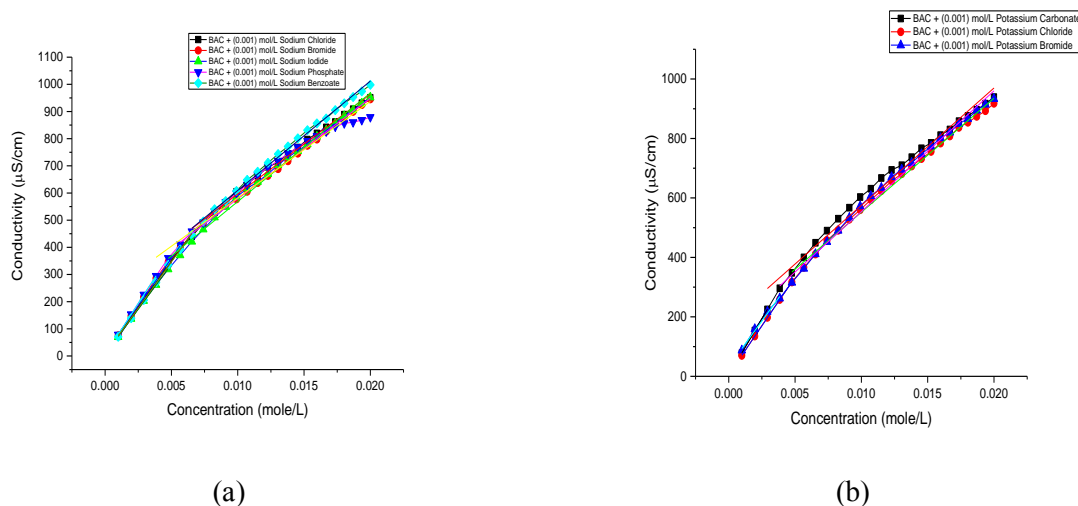

(a)

(b)

Figure 1. Conductivity vs concentration of BAC in different aqueous solutions from 0.001 mol/L (a) sodium salts, and (b) potassium salts at 298.15 $^°$K.
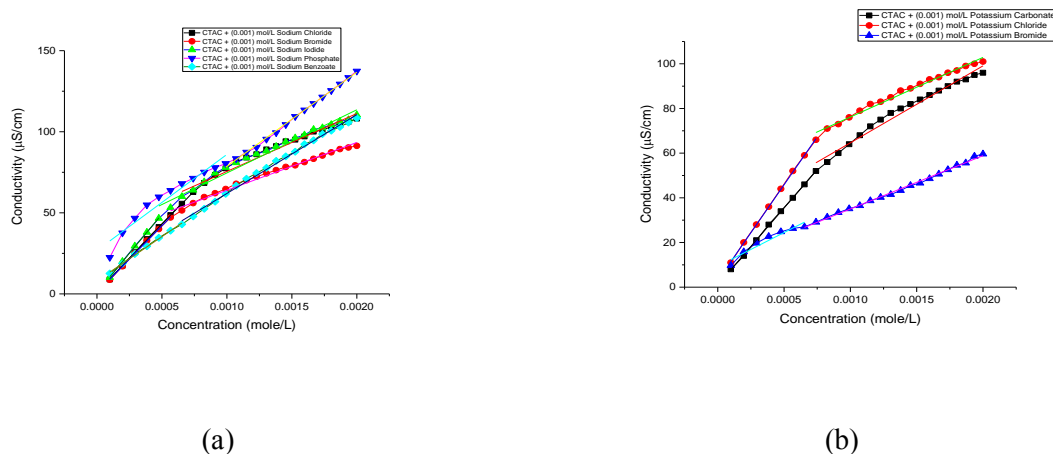

(a)

(b)

Figure 2. Conductivity vs concentration of CTAC in different aqueous solutions from 0.001 mol/L sodium salts, and (b) potassium salts at 298.15 $^°$K.

Generally, from **Figures 1 and 2** it was observed that the specific conductance increases with addition of salts. Such phenomenon can be explained due to addition of counter-ions (e.g. Na^+ and Cl^-) for carrying current.

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Table 2. CMC (mol/L) values for BAC in aqueous solution of salts under study at 298.15 °K from conductivity measurements.

Salt conc (mol/L)	CMC (mol/L)									
	KCl	KBr	K_2CO_3	NaCl	NaBr	NaI	Na_3PO_4	$(C_6H_5)COONa$	$MgSO_4$	$ZnSO_4$
0.00000	0.00525	0.00525	0.00525	0.00525	0.00525	0.00525	0.00525	0.00525	0.00525	0.00525
0.00100	0.00475	0.00382	0.00389	0.00503	0.00389	0.00347	0.00477	0.00482	0.00484	-
0.01000	0.00467	0.00374	0.00387	0.00497	0.00381	0.00292	0.00392	0.00469	0.00481	-
0.10000	0.00389	0.00292	0.00362	0.00476	0.00293	-	0.00384	0.00387	0.00452	-

Table 3. CMC (mol/L) values for CTAC in aqueous solution of salts under study at 298.15 °K from conductivity measurements.

Salt conc (mol/L)	CMC mol/L									
	KCl	KBr	K_2CO_3	NaCl	NaBr	NaI	Na_3PO_4	$(C_6H_5)COONa$	$MgSO_4$	$ZnSO_4$
0.00000	0.00100	0.00100	0.00100	0.00100	0.00100	0.00100	0.00100	0.00100	0.00100	0.00100
0.00100	0.00065	0.00056	0.00074	0.00074	0.00057	0.00048	0.00086	0.00060	0.00045	0.00092
0.01000	0.00064	0.00054	0.00071	0.00073	0.00057	0.00049	0.00083	0.00058	0.00045	0.00090
0.10000	0.00057	0.00048	0.00038	0.00057	0.00048	0.00038	0.00066	0.00047	0.00037	0.00069

The Critical micelle concentration of the two cationic surfactants as a function of salts concentration was showed in supplementary **Figures S1** and **S2**.

In water, the CMC of BAC and CTAC at 298.15 °K to be 0.00525 and 0.00100 mol/L respectively [22]. Also, the CMC values of the two surfactants aqueous solutions in the absence and presence of salts at room temperature are shown in **Table 2** and **3**. As the salt is added, the electrostatic repulsive force between ionic head groups of the surfactant molecules is reduced by shielding of micelle charge, so that spherical micelles are more closely packed by the surfactant ions, hence a decrease in the CMC values after adding salts [23].

The charge on the counter-ion plays significant role in the micellization phenomenon. Due to the synergistic effect, on increasing salt concentration, a decrease in CMC values of surfactants is observed. This can be understood by considering the positive and negative contributing factors in the micellization process. The primary driving force in micellization is the hydrophobic effect associated with the alkyl chain association [24], which promotes the release of water molecules and solvates the non-polar chain. Due to the hydrophobic effect or the assembly of the amphiphilic monomers, a net entropy increase in the system takes place. There is a balance between the electrostatic force among the amphiphilic head groups with their counter-ions and water at the micellar surface. Neutral ion pairs are formed by the positively charged head groups and negatively charged counter-ions in solution that are less hydrated than free ions, which ultimately leads to

the release of water into the bulk with the entropy increase. The more hydrophobic the counter-ion, the more strongly it interacts with an amphiphilic micellar interface (leading to stronger ion-pair formation), hence favouring micelle formation by reducing the CMC.

In general the CMC values for the two surfactants are found to be highest in the pure water then, addition of salts well known to lower the CMC as shown in **Tables 2** and **3.** We can summarized this decreasing in the following order: pure water > (0.001 M) aqueous solution of salts > (0.01 M) aqueous solution of salts > (0.1 M) aqueous solution of salts. This may be related to increasing the salt concentration reduces the electrostatic Debye screening length around the surfactant, which encourages the formation of longer micelles at equilibrium. This, in turn contributes to the changes in CMC [23,25] found that spherical micelles associated to form into rod-like micelles when salt concentration exceeded a threshold concentration.

The effect of alkali halide salts has been observed clearly in **Tables 2** and **3**, on the other hand the change in the accompanied halogen elements to the same alkali metal for its halide salts. Also, the same thing for the potassium halide salts the molecular weight and solubility increase in the following direction KCl < KBr and the CMC decrease in the opposite direction KCl > KBr. It was observed by [9,26,27] that the CMC of surfactant decreases in presence of NaBr and KCl. Similarly, the CMC of the two solution decreases in presence of NaBr. When NaBr is added in solution of BAC and CTAC counter-ion inserts in between the

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micelles hence decrease their force of repulsion between the micelles and CMC decreases. The trends of CMC for BAC and CTAC in presence of salts is in the order of CMC (NaCl) > CMC (NaBr) > CMC (NaI) and CMC (KCl) > CMC (KBr). The lattice energy (kJ/mol) of salts in the sequence: NaCl = 786 > NaBr = 747 > NaI = 704 and KCl =715 > KBr =682; while the ionization potential (eV) of salts in the sequence: NaCl =8.9 > NaBr = 8.4 > NaI = 7.6 and KCl = 8.3 >KBr = 8.0, [28]. Another important note was observed in case of sodium iodide aqueous solution when its concentration increases from 0.01 to 0.1 M, the CMC can't be detected for BAC surfactant.

It was observed that the CMC decreases with the increase in radii of counter-ions as in the order radii (A°) of NaCl = 5.6405 < NaBr = 5.9732 < NaI = 6.476 and KCl = 6.290 < KBr = 6.600. Also the CMC decreases with the increase in the internuclear separation (A°) of NaCl = 2.820 < NaBr = 2.987 < NaI = 3.238 and KCl = 3.146 < KBr = 3.300, the results was found to be agree with previous literatures [29–32].

While in case of sulphates salts solution, the CMC decrease as the atomic radii of related metal decrease, then molecular weight of the salt, for example, zinc and magnesium sulphates salts. The molecular weight increases as the following order: $MgSO_4$ < $ZnSO_4$ and the CMC decrease in the same order, probably this may be the high solubility of zinc sulphates than magnesium sulphates salt in aqueous solutions. Salts decrease the CMC in the order: $ZnSO_4$ < $MgSO_4$. Here Zn^{++} is least effective in decreasing the CMC due to small size and large hydrated radius and would act as a water- structure promoter decreasing the availability of water to the micelles. Therefore, upon addition of $ZnSO_4$ and $MgSO_4$ in cetyl trimethyl ammonium chloride, $MgSO_4$ is more effective in reducing the CMC of CTAC. The results has been agree with previous study [33]. The previous case is only for CTAC surfactant solution, while in BAC surfactant solution and when adding the zinc sulphates aqueous solution to it the CMC can't be detected.

Again, when the following salt solutions: $(C_6H_5)COONa$, Na_3PO_4 and K_2CO_3 had been added to the two surfactant solutions, it interacted strongly with water and salt out the surfactant molecules, and micellization is favoured at lower cmc values. The result was agree with a previous literature [5]. **Table 4** shows the variation of the critical micelle concentration values in different solutions (i.e. dye-

surfactant, and surfactant-surfactant) using the conductivity method as mentioned in the experimental section [22].

Table 4.CMC (mol/L) values for BAC and CTAC in different aqueous solutions at 298.15 ^{0}K using conductivity method.

Solution		BAC	CTAC
Concentration (mol/L)		CMC (mol/L)	
Aqueous	-	*0.00525* *	*0.00100* *
MB	0.00003	0.00698	0.00141
BAC	0.00100	-	0.00080
	0.01000	-	0.00107
CTAC	0.00010	0.00361	-
	0.01000	0.00442	-

* Values in bold italic for both two surfactants in pure water at 298.15 ^{0}k were from previous study [22]

From **Table 4** it was observed that in case of methylene blue + surfactants solutions, the critical micelle concentration of the two surfactants increased with addition of dye. Such phenomenon can be explained due to addition of counter-ions (e.g., Na^+ and Cl^-) for the carrying current.

On the other hand, when the cationic surfactant (i.e. BAC) was added stepwise to aqueous solution of another cationic surfactant (i.e. CTAC) with two concentrations before and after it's CMC value, the critical micelle concentration of the cationic surfactant (BAC) was decreased. This may be because these systems are comprised of similarly charged surfactants and the bivalent ions possess a higher degree of counter-ion binding which, leading to greater charge neutralization and less electrostatic repulsion between the polar head groups [34].

3.2. Thermodynamic parameters of Micellization

The degree of ionization in the micelle (α) and the degree of counter-ion binding, β = (1- α) of the two surfactants as a function of mole fraction of alcohol at different temperatures was suggested as in the following **equation (1)** [35]

$$\alpha = S_2/S_1 \dots\dots\dots (1)$$

Where S_2/S_1, the ratio of slopes of post and pre micelle regions and subsequently β was calculated as, β = (1 − α). The slopes were estimated from the linear plots of conductivity versus concentration of surfactants. The values of α and β are recorded in **Tables 5** and **6.**

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Table 5. The degree of ionization (α) of BAC and CTAC in aqueous solution of salts at room temperature 298.15 °K.

Solvent mixtures	Salt conc (mol/L)	α									
		KCl	KBr	K₂CO₃	NaCl	NaBr	NaI	Na₃PO₄	(C₆H₅)COONa	MgSO₄	ZnSO₄
BAC	0.0000	0.566	0.566	0.566	0.566	0.566	0.566	0.566	0.566	0.566	0.566
	0.0010	0.586	0.697	0.501	0.546	0.523	0.606	0.457	0.601	0.831	-
	0.0100	0.616	0.679	0.545	0.584	0.558	0.638	0.491	0.614	0.844	-
	0.1000	0.915	0.508	0.978	0.956	0.912	-	0.833	0.743	0.968	-
CTAC	0.0000	0.337	0.337	0.337	0.337	0.337	0.337	0.337	0.337	0.337	0.337
	0.0010	0.356	0.703	0.520	0.401	0.359	0.405	0.902	0.889	0.888	0.884
	0.0100	0.648	0.562	0.757	0.676	0.649	0.683	0.915	0.866	0.926	0.939
	0.1000	0.939	0.421	0.994	0.951	0.940	0.961	0.929	0.842	0.965	0.994

Table 6. The degree of counter-ion binding, β= (1- α) of BAC and CTAC in aqueous solution of salts at room temperature 298.15 °K.

Solvent mixtures	Salt conc (mol/L)	β									
		KCl	KBr	K₂CO₃	NaCl	NaBr	NaI	Na₃PO₄	(C₆H₅)COONa	MgSO₄	ZnSO₄
BAC	0.0000	0.434	0.434	0.434	0.434	0.434	0.434	0.434	0.434	0.434	0.434
	0.0010	0.414	0.303	0.499	0.454	0.477	0.394	0.543	0.399	0.169	-
	0.0100	0.384	0.321	0.455	0.416	0.442	0.362	0.509	0.386	0.156	-
	0.1000	0.085	0.492	0.022	0.044	0.088	-	0.167	0.257	0.032	-
CTAC	0.0000	0.663	0.663	0.663	0.663	0.663	0.663	0.663	0.663	0.663	0.663
	0.0010	0.644	0.297	0.480	0.599	0.641	0.595	0.098	0.111	0.112	0.116
	0.0100	0.352	0.438	0.243	0.324	0.351	0.317	0.085	0.134	0.074	0.061
	0.1000	0.061	0.579	0.006	0.049	0.060	0.039	0.071	0.158	0.035	0.006

The thermodynamic parameter of micellization were obtained using the following equation [36]:

$$\Delta G^0_{mic} = (2- \alpha) RT \ln [CMC] \quad \dots\dots\dots\dots (2)$$

Where α is the degree of ionization in the micelle, R is the gas constant and T is the absolute temperature. The standard free energy change (ΔG^0_{mic}) of micellization process of the surfactant was calculated using **equation (2)**. The values of (ΔG^0_{mic}) are recorded in **Table7.**

Table 7. The standard free energy change (ΔG^0_{mic}) of BAC and CTAC in aqueous solution of salts at room temperature 298.15 °K.

Solvent mixtures	Salt conc (mol/L)	ΔG^0_{mic} (kJ/mol)									
		KCl	KBr	K₂CO₃	NaCl	NaBr	NaI	Na₃PO₄	(C₆H₅)COONa	MgSO₄	ZnSO₄
BAC	0.0000	-18.66	-18.66	-18.66	-18.66	-18.66	-18.66	-18.66	-18.66	-18.66	-18.66
	0.0010	-18.75	-17.99	-20.61	-19.07	-20.32	-19.57	-20.44	-18.51	-15.44	-
	0.0100	-18.41	-18.29	-20.04	-18.62	-19.91	-19.71	-20.73	-18.43	-15.30	-
	0.1000	-14.92	-21.58	-14.24	-13.84	-15.73	-	-16.09	-17.32	-13.82	-
CTAC	0.0000	-28.47	-28.47	-28.47	-28.47	-28.47	-28.47	-28.47	-28.47	-28.47	-28.47
	0.0010	-29.90	-24.05	-26.44	-28.57	-30.39	-30.23	-19.22	-20.44	-21.23	-19.33
	0.0100	-24.64	-26.85	-22.35	-23.73	-25.04	-24.88	-19.08	-20.93	-20.54	-18.44
	0.1000	-19.66	-29.91	-19.64	-19.45	-20.09	-20.25	-19.45	-21.99	-20.27	-18.17

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Table 8. Thermodynamic parameters for micellization (α, β and ΔG_{mic}^{0}) of BAC and CTAC in different aqueous solutions at room temperature 298.15 °K.

Type of Solution	Solution Concentration mol/L	α		β		ΔG_{mic}^{0} (kJ/mol)	
		BAC	CTAC	BAC	CTAC	BAC	CTAC
Water	-	0.556	0.337	0.444	0.663	-18.38	-27.39
MB	0.00003	0.495	0.420	0.505	0.580	-18.52	-25.7
BAC	0.00100	-	0.434	-	0.566	-	-27.66
	0.01000	-	0.606	-	0.566	-	-23.64
CTAC	0.00010	0.743	-	0.257	-	-17.52	-
	0.01000	0.985	-	0.257	-	-13.63	-

From **Tables 7-8**, the values of ΔG_{mic}^{0}, were found to be negative in all the cases, showing the spontaneity of the micellization process, indicating that the increase in the concentration of salts makes the process more spontaneous, this implies that the surfactant/electrolyte solutions are more stable.

3.3. Refractive index and surface tension measurements

The Refractive index and surface tension of the (salt + surfactant), (cationic dye + surfactant) and (surfactant + surfactant) mixed systems in aqueous solvent has been measured experimentally at room temperature (298.15 °K) as described in the experimental section. To estimate the CMC of the two surfactants in the previous mixed solution at room temperature, the relation between refractive index and surface tension versus concentration for the surfactants were done. There CMC values has been collected in **Tables 10**. Depending on the surface tension data, some surface properties of surfactants including excess surface concentration (Γ_{max}), minimum area per molecule (A_{min}) and Surface pressure (π_{CMC}) were also calculated and discussed. The data was collected in **Table 9.**

At the air-liquid interface, the term of maximum surface excess concentration (Γ_{max}) value was calculated using Gibb's isotherm [37]:

$$\Gamma_{max} = -1/2.303 \, nRT \, (dy/d \log C)_{T} \quad \dots\dots\dots\dots (3)$$

Where n is referring to the number of particles furnished by each molecule of the surfactant in the solution, for these surfactants the values n=2, R is the ideal gas constant. The term $(dy/d \log C)_{T}$ represents the slope of the relationship between surface tension versus log C at temperature T. The minimum area per molecule (A_{min}) of surfactant at the liquid-air interface (in nm^2) was calculated using the following equation:

$$A_{min} = 10^{14}/N\Gamma_{max} \quad \dots\dots\dots\dots (4)$$

Where, N is Avogadro's number.

Surface pressure at CMC (π_{CMC}) or the effectiveness of surface tension, an index of surface tension reduction at CMC, has been calculated using the following equation [1,38] :

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad \dots\dots\dots\dots (5)$$

Where γ_0 = surface tension of water and γ_{CMC} = surface tension of surfactant solution at CMC point

Table 9. Surface physico-chemical properties of BAC and CTAC in methyle blue aqueous solutions at room temperature 298.15 °K.

Surfactant	Γ_{max}	A_{min}	π_{CMC}
	mol/cm^2	10^{-3} nm^2/molecule	10^{-8} dyne/cm
BAC	30.35	3.26	5.10
BAC in 3x10^{-5} MB $_{(aq)}$	2.53	6.56	20.66
CTAC	31.28	2.47	6.71
CTAC in 3x10^{-5} MB $_{(aq)}$	1.96	8.49	19.93

At the interface of solution, the surfactant molecule (BAC and CTAC) was adsorbed, in spite of a low concentration of surfactant. As a result of this the surface tension of water is decreased. The surfactant adsorption can be explained according to different interactions (i.e. hydrogen bonding, electrostatic interaction, hydrophobic effect, Van der Waals interaction etc.) It is known that as the hydrophobic chain length of surfactants increase the hydrophobicity of surfactants will increase. So that, the surfactant monomers prefer to run away into the air-liquid interface. Therefore, the parameter (Γ_{max})

in **Table 9** reflected that the surface tension of the (BAC/MB and CTAC/MB) mixtures is reduced more than that of BAC and CTAC in water when MB monomers get into solution. On the other hand, the minimum area (A_{min}) and surface pressure at CMC of a surfactant molecule (BAC or CTAC) in aqueous solution of methylene blue was increase than in pure water. This may be due to addition of counter-ions (e.g., Na^+ and Cl^-) and then increase the hydrogen bond [39–41].

3.4. Ultra Violet measurements

The critical micelle concentration of the two surfactants in absence and presence of cationic dye methylene blue was measured using the relation between the intensity of the absorbance and the concentration of surfactant in UV–visible range (200 – 400 nm) and (400 – 750 nm) respectively, **Figures 3** and **4** and supplementary summarized this relation. To estimate the CMC values of the two surfactants BAC and CTAC in water and in the aqueous solution of dye, the relation of the measured absorbance versus the surfactant concentration was done as presented in **Figures 3** and **4**. The CMC values are collected in **Table 10**.
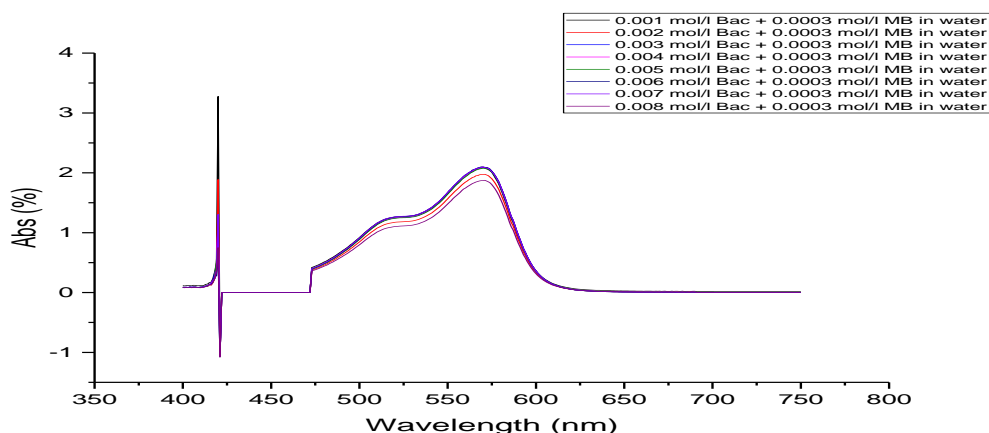
Figure 3. UV absorbance of different concentration for BAC in (3×10^{-5} mol/L) aqueous solution of MB at 298.15 °K.
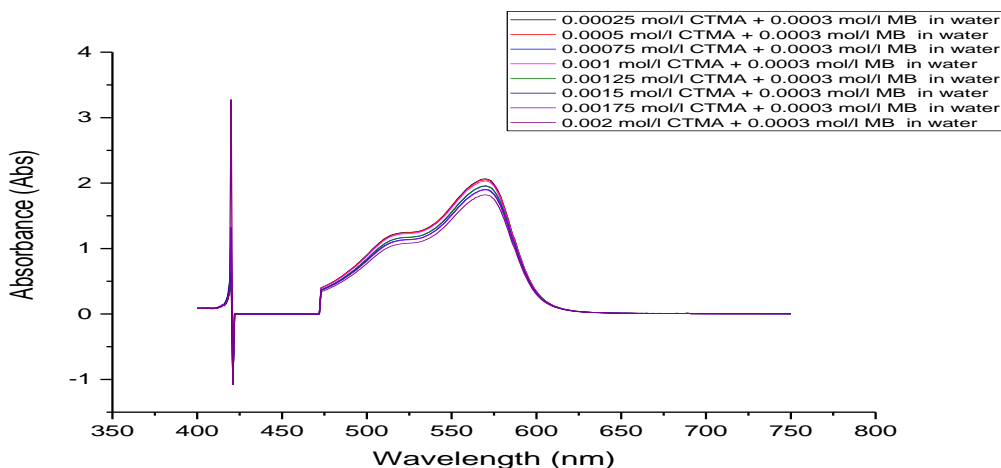

Figure 4. UV absorbance of different concentration for CTAC in (3×10^{-5} mol/L) aqueous solution of MB at 298.15 °K.

The CMC values were checked by taking double differential of absorbance values with respect to concentration using origin inbuilt functions and the fitting is nonlinear using the nonlinear fitting tool of the software. Gaussian distribution function was applied and the maximum was taken as the CMC value [35], the results were collected in **Table 10**.

From **Table 10**, the value of CMC for the two surfactants (BAC and CTAC) was found to be increasing when the cationic dye (methylene blue) was added to their aqueous solutions.

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A hypochromic shift occurred to the maximum wavelength of free methylene blue from 653 nm to 570 nm due to the formation of trimer MB [42]. The trimer MB occurred due the electrostatic repulsion between the similarly charged surfactant and MB molecules, the tendency to form free MB increases by decreasing the electrostatic repulsion and vice versa. By increasing the cationic surfactant concentration, the repulsion between it and the MB increased, so the concentration of trimer MB also increased until it reached the CMC value, then the process was reversed [43].

3.5. Comparison between CMC values using different methods

In comparing the CMC values, for the two surfactants under study and in (0.01 mol/L $MgSO_4$ and NaCl aqueous solutions), ($3x10^{-5}$ mol/L MB) and different concentration of surfactants at 298.15 $^\circ$K, determined experimentally using conductivity, refractive index, surface tension and UV spectroscopy techniques as shown in **Figures 5-8** as an example, it was found that there is a good agreement between the CMC values resulted in the three techniques (**Table 10**).Also it was found that the experimentally CMC values, obtained from the three techniques are in good agreement with that values in literatures [44,45].

Table 10.CMC (mol/L) values for BAC and CTAC in aqueous solution of NaCl and $MgSO_4$ as example at 298.15 $^\circ$K using different methods.

Item	CMC mol/L			
	Molar Conductance	Refractive Index	Surface Tension	UV spectroscopy
BAC *	*0.00525*	*0.00566*	*0.00579*	*0.00567*
BAC + $MgSO_4$	0.00484	0.00482	0.00476	-
BAC + NaCl	0.00503	0.00518	0.00516	-
BAC + MB	0.00698	0.00693	0.00698	0.00650
BAC + 0.00010 CTAC	0.00361	0.00361	-	-
BAC + 0.01000 CTAC	0.00442	0.00476	-	-
CTAC *	*0.00100*	*0.00115*	*0.00130*	*0.00128*
CTAC + $MgSO_4$	0.00045	0.00048	0.00048	-
CTAC + NaCl	0.00074	0.00077	0.00074	-
CTAC + MB	0.00140	0.00141	0.00140	0.00142
CTAC + 0.00100 BAC	0.00080	0.00081	-	-
CTAC + 0.01000 BAC	0.00107	0.00070	-	-

* Values in bold italic for both two surfactants in pure water at 298.15 $^\circ$k were from previous study [22]
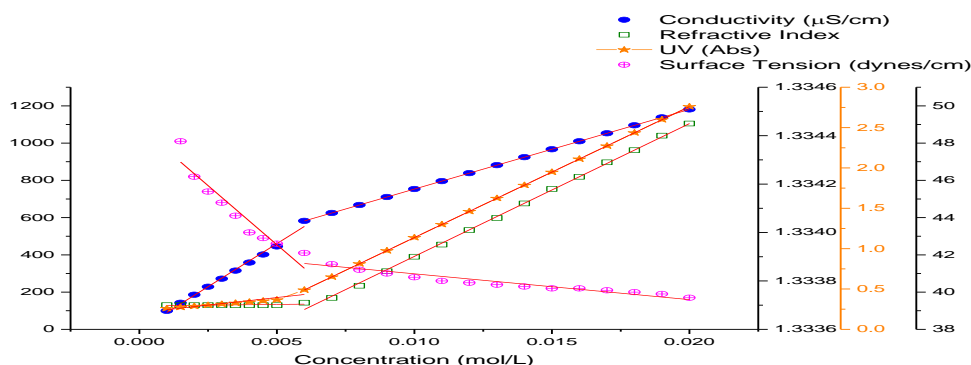

Figure 5. CMC values of BAC in water at 298.15 $^\circ$K using different methods.
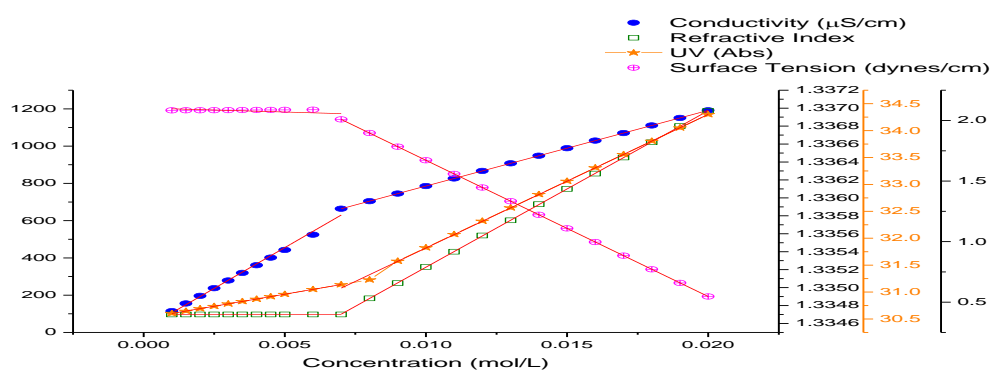
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Figure 6. CMC values of BAC in (3×10^{-5} mol/L) aqueous solution of MB at 298.15 $^\circ$K using different methods.
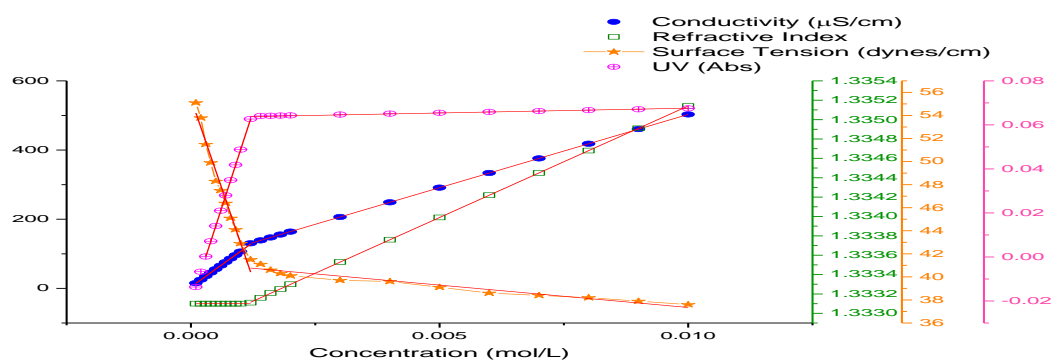

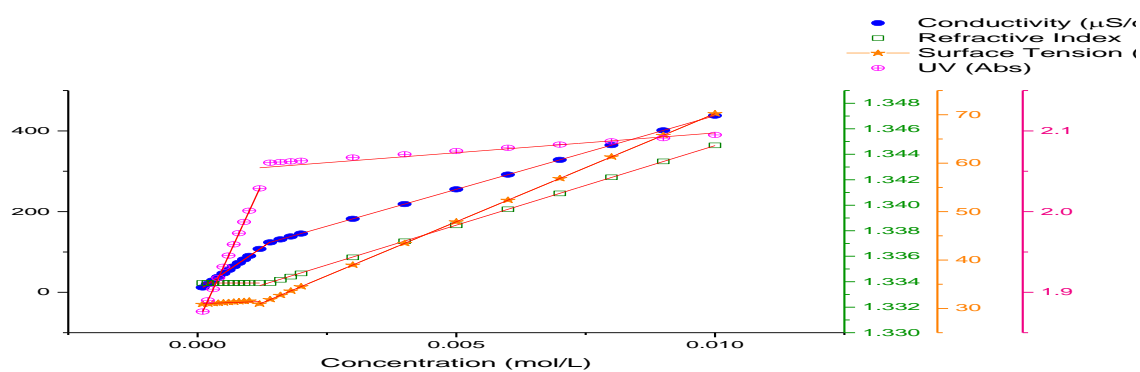**Figure 7.** CMC values of CTAC in water at 298.15 $^\circ$K using different methods.

Figure 8. CMC values of CTAC in (3×10^{-5} mol/L) aqueous solution of MB at 298.15 $^\circ$K using different methods.

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3.6. Hydrophilic-Lipophilic Balance (HLB) Concept

The HLB values represent an empirical numerical correlation of the emulsifying and solubilizing properties of different surface-active agents. HLB values of individual surfactant molecules can be calculated applying the Davies **equation (6)** [46]:

$$HLB = \Sigma(\text{Hydrophilic group contributions}) - \Sigma(\text{Hydrophobic group contributions}) + 7 \quad \ldots\ldots \text{ (6)}$$

The HLB values of the two surfactants were recorded in **Table 11.**

Table 11. Hydrophilic-Lipophilic Balance (HLB) of BAC and CTAC using Davies equation.

Surfactant	HLB Value
Alkyl Benzyl Dimethyl Ammonium Chloride (BAC)	20.5
Cetyl Trimethyl Ammonium Chloride (CTAC)	21.4

3.7. Modeling study

The following Setschenow equation was applied to describe the effect of adding salts on the micelle size and shape of the two surfactants [47].

$$\log ((CMC)_\circ /(CMC)) = kC \ldots\ldots (7)$$

where $(CMC)_\circ$ and (CMC) are the CMC of the studied surfactants in water and in the electrolyte solution of concentration C respectively, while k is the Setschenow constant. Setschenow constant is a measurable parameter for the effect of the salt on the CMC value. The plots of $\log ((CMC)/(CMC)_\circ)$ versus C in the present study for the studied surfactants under study, **Figures 9 and 10**, suggest that a the following extended Setschenow equation can be applied:

$$\log ((CMC)_\circ /(CMC)) = k_1 C + k_\circ \ldots\ldots\ldots. \text{ (8)}$$

The Setschenow parameters; $k_\circ$ and k_1, of **Equation 8** were evaluated and reported in **Table 12** and shown in **Figures 9 and 10**.

The positive values of k_1 indicate a positive effect of the salt's concentration on the CMC value, i.e. decrease in the CMC value. **Figure 11** shows that the values of k_1 adequately represent the experimental CMC of the surfactants under study where the same trend of the change in the CMC was observed. It was found that the difference between the parameters is sensibly constant. This indicates that the determined parameters are additive. **Figure 11** and **Table 12**, also show that the order of the salt effect is inversely proportional to the order of CMC values in different salts. This means that as the CMC increase the value of k_1 decrease and vice versa.
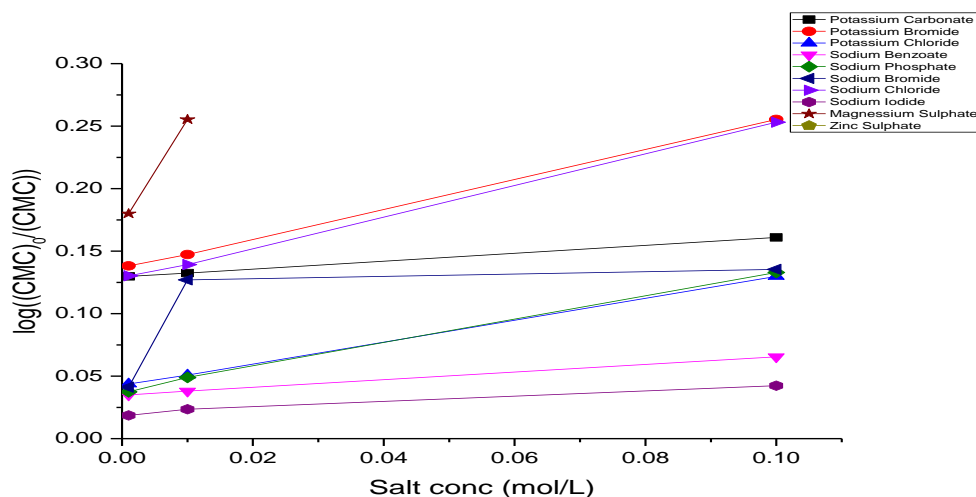

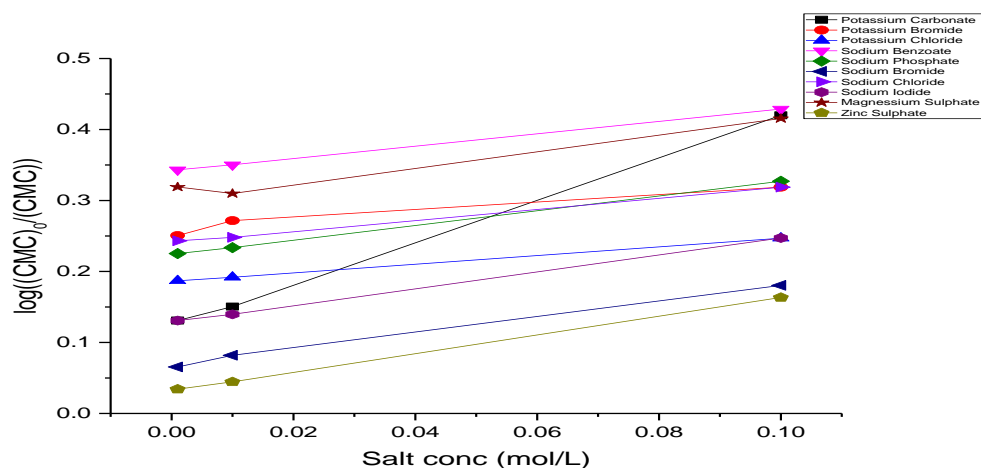**Figure 9.** Setschenow parameters of BAC in aqueous solution of different salts concentrations at 298.15 °K.

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Figure 10. Setschenow parameters of CTAC in aqueous solution of different salts concentrations at 298.15 $^\circ$K.

Table 12. The Setschenow parameters for BAC and CTAC in different salts.

| Salt | BAC | | | CTAC | | |
| | Model Equation: $y = k_1x + k_0$; R^2 | | | Model Equation: $y = k_1x + k_0$; R^2 | | |
	K_o	K_1	R^2	K_o	K_1	R^2
K_2CO_3	0.1296	0.3183	0.9997	0.1237	2.9613	0.9993
KBr	0.1362	1.1850	0.9999	0.2560	0.6325	0.9790
KCl	0.0423	0.8785	1.0000	0.1873	0.5692	0.9993
$MgSO_4$	0.0378	0.9485	0.9990	0.2233	1.0484	0.9979
$(C_6H_5)COONa$	0.0790	0.6060	0.4073	0.0668	1.1388	0.9983
Na3PO4	0.1279	1.2530	0.9997	0.2400	0.7844	0.9932
NaBr	0.0199	0.2284	0.9842	0.1274	1.1648	0.9987
NaCl	-	-	-	0.3264	2.2436	0.9979
NaI	0.0350	0.3001	1.0000	0.3421	0.8935	0.9932
$ZnSO_4$	-	-	-	0.0340	1.2702	0.9998
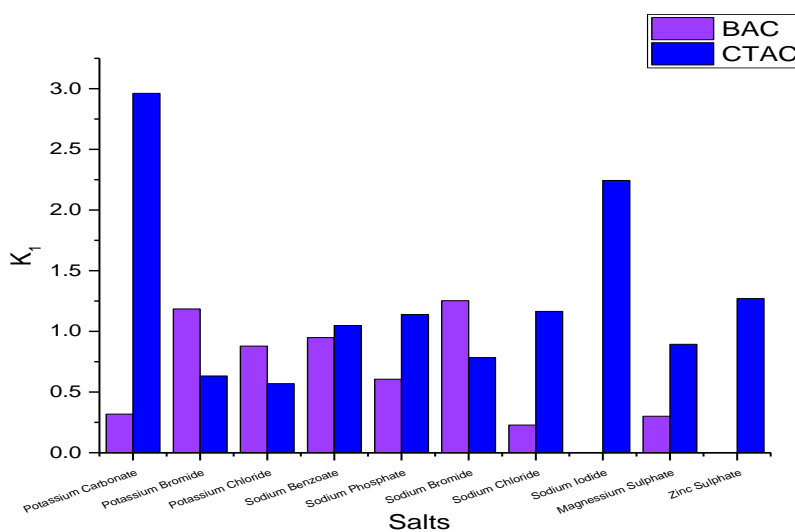
Figure 11. Setschenow constant (K_1) values of BAC and CTAC in aqueous solutions of different salts at 298.15 $^\circ$K.

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4. Conclusion

The effect of adding different salts on the CMC of Alkyl Benzyl Dimethyl Ammonium Chloride (BAC) and Cetyl Trimethyl Ammonium (CTAC)surfactants in aqueous solvent, has been determined experimentally at room temperatures (298.15 $^{\circ}$K) using the conductivity measurements. The CMC of the two surfactants was found to be decrease as the concentration of salts increase. It was found good agreement between the observed values in the present study with a recent study. Depending on the conductivity data of (BAC) and (CTAC) the thermodynamic parameters (ΔG°, α and β) of the micellization processes were determined. The results indicate that the change in free energy of micellization was found to be negative in all the cases, showing the spontaneity of the micellization process. The Hydrophilic-Lipophilic Balance (HLB) values of the two surfactants (BAC) and (CTAC) were determined using Davies's equation. The CMC value of the two cationic surfactants in water and in the presence of three aqueous molar concentration of different salts was modelled using the Setschenow relationship. The difference between the Setschenow parameters is sensibly constant, this indicates that the order of the salt effect is inversely proportional to the order of CMC values in different salts.

5. Conflicts of interest

In accordance with our policy on Conflict of interest please ensure that a conflicts of interest statement is included in your manuscript here. Please note that this statement is required for all submitted manuscripts. If no conflicts exist, please state that "There are no conflicts to declare".

6. Formatting of funding sources

List funding sources in a standard way to facilitate compliance to funder's requirements.

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Collate acknowledgements in a separate section at the end of the article before the references and do not, therefore, include them on the title page, as a footnote to the title or otherwise. List here those individuals who provided help during the research (e.g.,

providing language help, writing assistance or proof reading the article, etc.).

8. References

[1] T. Tadros, Encyclopedia of Colloid and Interface Science, Springer, Berlin Heidelberg, 2013. https://doi.org/10.1007/978-3-642-20665-8.

[2] M.F. Ahmed, M. Abdul Rub, M.T.R. Joy, M.R. Molla, N. Azum, M. Anamul Hoque, Influences of NaCl and Na_2SO_4 on the Micellization Behavior of the Mixture of Cetylpyridinium Chloride + Polyvinyl Pyrrolidone at Several Temperatures, Gels. 8 (2022) 1–14. https://doi.org/10.3390/gels8010062.

[3] A.J. Ležaić, N. Pejić, J. Goronja, L. Pavun, D. Đikanović, A. Malenović, Micellar Properties of Cetyltrimethylammonium Bromide in an Acetonitrile-Water Mixture: Conductometric and Fluorescence Studies, Maced. J. Chem. Chem. Eng. 40 (2021) 277–287. https://doi.org/10.20450/MJCCE.2021.2394.

[4] M. Bali, O. Masalci, Interactions of cationic surfactants with polyvinylpyrrolidone (PVP): Effects of counter ions and temperature, J. Mol. Liq. 303 (2020) 112576. https://doi.org/10.1016/j.molliq.2020.112576.

[5] S. Mahbub, M.A. Rub, M.A. Hoque, M.A. Khan, D. Kumar, Micellization behavior of cationic and anionic surfactant mixtures at different temperatures: Effect of sodium carbonate and sodium phosphate salts, J. Phys. Org. Chem. 32 (2019) 1–17. https://doi.org/10.1002/poc.3967.

[6] N. Patra, D. Ray, V.K. Aswal, S. Ghosh, Exploring Physicochemical Interactions of Different Salts with Sodium N-Dodecanoyl Sarcosinate in Aqueous Solution, ACS Omega. 3 (2018) 9256–9266. https://doi.org/10.1021/acsomega.8b00718.

[7] B.H. Lee, Effects of Various Alcohols and Salts on the Mixed Micellization of Cationic Surfactant (CPC) with Nonionic Surfactant (TX-100), Colloids Interface Sci. Commun. 19 (2017) 1–4. https://doi.org/10.1016/j.colcom.2017.05.001.

[8] K. Jha, A. Bhattarai, S.K. Chatterjee, Determination of critical micelle concentration of cetyltrimethylammonium bromide in presence and absence of KCl and NaCl in aqueous media at room temperature by viscosity measurement, Bibechana. 11 (2014) 131–135.

_____

https://doi.org/10.3126/bibechana.v11i0.1039 2.

[9] S. Shah, S. Chatterjee, A. Bhattarai, Micellization behaviour of cetyltrimethylammonium bromide in methanol-water mixed solvent media in absence and in the presence of a salt at (308 . 15 , 318 . 15 and 323 . 15) K by conductometry, Adv. J. Phys. Sci. 2 (2013) 10–17.

[10] C. Adhikari, G. Shrivastav, A. Bhattarai, Micellization Behavior of Cetyltrimethylammonium bromide in Presence and Absence of Na_2SO_4 and $MgSO_4$ in Aqueous media, Bibechana. 14 (2016) 77–85. https://doi.org/10.3126/bibechana.v14i0.1587 1.

[11] A. Bhattarai, K. Chatterjee, K. Jha, Density and partial molar volume of Cetyltrimethylammonium Bromide in the presence and absence of KCl and NaCl in aqueous media at room temperature, Phys. Chem. 5 (2015) 1–5. https://doi.org/10.5923/j.pc.20150501.01.

[12] S. Amjad, S. Shaukat, H.M.A.U. Rahman, M. Usman, Z.H. Farooqi, M.F. Nazar, Application of anionic-nonionic mixed micellar system for solubilization of methylene blue dye, J. Mol. Liq. 369 (2023) 120958. https://doi.org/10.1016/J.MOLLIQ.2022.120 958.

[13] S. Noor, M.B. Taj, A. Ashar, Solubilization of cationic dye in single and mixed micellar media, J. Mol. Liq. 330 (2021) 115613. https://doi.org/10.1016/j.molliq.2021.115613.

[14] P. Shah, A. Bhattarai, D. Kumar, Interaction of methylene blue with SDS in the premicellar solution of CPC in the aqueous and methanol-water system, Colloids Surfaces A Physicochem. Eng. Asp. 648 (2022) 129091. https://doi.org/10.1016/j.colsurfa.2022.12909 1.

[15] P. Shah, N. Jha, A. Bhattarai, Physicochemical Studies on the Interaction between Sodium Dodecyl Sulfate and Methylene Blue in Methanol-Water Mixed Solvent Media, J. Chem. 2020 (2020) 1–13. https://doi.org/10.1155/2020/5292385.

[16] A. Gadhave, Determination of Hydrophilic-Lipophilic Balance Value, Int. J. Sci. Res. 3 (2014) 573–575.

[17] C. Griffin, Calculation of HLB values of non-ionic surfactants, J. Soc. Cosmet. Chem. 5 (1954) 249–256.

[18] M. Marasco, A Titration Method for the Determination of Silver in Photographic Preparations, Ind. Eng. Chem. 16 (1924) 945–946. https://doi.org/10.1021/ie50177a033.

[19] E. Lavagnini, J.L. Cook, P.B. Warren, C.A. Hunter, Systematic Parameterization of Ion–Surfactant Interactions in Dissipative Particle Dynamics Using Setschenow Coefficients, J. Phys. Chem. B. 126 (2022) 2308–2315. https://doi.org/10.1021/acs.jpcb.2c00101.

[20] W. Kunz, P. Lo Nostro, B.W. Ninham, The present state of affairs with Hofmeister effects, Curr. Opin. Colloid Interface Sci. 9 (2004) 1–18. https://doi.org/10.1016/j.cocis.2004.05.004.

[21] J. Setschenow, Über die Konstitution der Salzlösungen auf Grund ihres Verhaltens zu Kohlensäure, Zeitschrift Für Phys. Chemie. 4U (1889) 117–125. https://doi.org/10.1515/zpch-1889-0409.

[22] F. El-Dossoki, E. Gomaa, O. Hamza, Solvation Thermodynamic Parameters for Alkyl Benzyl Dimethyl Ammonium Chloride and Cetyl Trimethyl Ammonium Chloride Surfactants in Water and Alcoholic-Water Solvents, J. Chem. Eng. Data. 64 (2019) 4482–4492. https://doi.org/10.1021/acs.jced.9b00527.

[23] J. Aslam, U.S. Siddiqui, W.H. Ansari, Kabir-Ud-Din, Micellization studies of dicationic gemini surfactants (m-2-m Type) in the presence of various counter- and Co-ions, J. Surfactants Deterg. 16 (2013) 693–707. https://doi.org/10.1007/s11743-013-1453-5.

[24] D. CHAPMAN, The Hydrophobic Effect: Formation of Micelles and Biological Membranes (2nd Edition), 2nd ed., Wiley, New York, 1981. https://doi.org/10.1042/bst0090178.

[25] K. Fujio, The Salt-Induced Sphere-Rod Transition of Micelles of 1-Tetradecylpyridinium Bromide in Aqueous NaBr Solutions, Bull. Chem. Soc. Jpn. 71 (1998) 83–89. https://doi.org/10.1246/bcsj.71.83.

[26] W. Malik, S. Saleem, Effect of additives on the critical micelle concentration of some polyethoxylated nonionic detergents, J. Am. Oil Chem. Soc. 45 (1968) 670–672. https://doi.org/10.1007/BF02541253.

[27] T. Niraula, A. Bhattarai, S. Kumar, Conductometric studies on the effect of NaBr on the micellization of sodium dodecyl sulphate (SDS) in pure water and methanol-water mixed solvent media at different temperatures, Nepal Biol. Soc. (2013) 62–74.

[28] T.P. Niraula, S.K. Chatterjee, A. Bhattarai, Micellization of sodium dodecyl sulphate in

_____

presence and absence of alkali metal halides at different temperatures in water and methanol-water mixtures, J. Mol. Liq. 250 (2018) 287–294. https://doi.org/10.1016/j.molliq.2017.12.014.

[29] J. Donnay, Crystal data : determinative tables. Vol. IV: Inorganic compounds 1967-1969, 3rd ed., U.S. Department of Commerce, Washington DC, 1978.

[30] P. Mukerjee, K.J. Mysels, P. Kapauan, Counterion specificity in the formation of ionic micelles-size, hydration, and hydrophobic bonding effects, J. Phys. Chem. 71 (1967) 4166–4175. https://doi.org/10.1021/j100872a702.

[31] E.D. Goddard, O. Harva, T.G. Jones, The effect of univalent cations on the critical micelle concentration of sodium dodecyl sulphate, Trans. Faraday Soc. 49 (1953) 980–984. https://doi.org/10.1039/tf9534900980.

[32] F.P. Boer, T.H. Jordan, X-ray crystallography Experiment: Powder patterns for alkali halides, J. Chem. Educ. 42 (1965) 76–81. https://doi.org/10.1021/ed042p76.

[33] A. Bhattarai, K. Limbu, Conductance of sodium dodecyl sulphate in presence and absence of Na_2SO_4, Sci. World. 12 (2014) 41–43.

[34] N. Azum, K.A. Alamry, S.B. Khan, M.A. Rub, A.M. Asiri, Y. Anwar, Synergistic interaction between anionic and nonionic surfactant: Application of the mixed micelles templates for the synthesis of silver nanoparticles, Int. J. Electrochem. Sci. 11 (2016) 1852–1867.

[35] J. Goronja, A. Janosevic-Lezaic, B. Dimitrijevic, A. Malenovic, D. Stanisavljev, N. Pejic, Determination of critical micelle concentration of cetyltrimethylammonium bromide: Different procedures for analysis of experimental data, Hem. Ind. 70 (2016) 485–492. https://doi.org/10.2298/HEMIND150622055 G.

[36] Z. Khan, M.A. Malik, S.A. AL-Thabaiti, A. Alshehri, F. Nabi, Micellization and thermodynamic properties of cationic surfactant cetyltrimethylammonium bromide in non-aqueous mixture of lauric acid, Int. J. Electrochem. Sci. 12 (2017) 4528–4542. https://doi.org/10.20964/2017.05.53.

[37] T.S. Banipal, H. Kaur, P.K. Banipal, Investigations on micellization and surface properties of sodium dodecyl sulfate in aqueous solutions of triflupromazine hydrochloride at different temperatures, J. Mol. Liq. 218 (2016) 112–119.

[38] Z. Ettarhouni, F. Elarbei, A. Jangher, L. Abusen, Determination of CMC and interfacial properties of anionic (SDS) and cationic (CPB) surfactants in aqueous solutions, Am. J. Eng. Res. 9 (2020) 118–126.

[39] L. Qin, X.H. Wang, Surface adsorption and thermodynamic properties of mixed system of ionic liquid surfactants with cetyltrimethyl ammonium bromide, RSC Adv. 7 (2017) 51426–51435. https://doi.org/10.1039/c7ra08915e.

[40] A.A. El Feky, M.N. Shalaby, O.A.A. El-Shamy, S.A. Selim, S.A. Selim, Surface Activity And Adsorption Of Some Surfactants At Aqueous / Air Interface At Different Temperatures, Int. J. Sci. Technol. Res. 5 (2016) 8. www.ijstr.org.

[41] R.S. Abdel Hameed, M. AlElaimi, M.T. Qureshi, O.A. Farghaly, M.F.H. Abd el-Kader, Green synthesis for nonionic surfactants from poly (ethyleneterphthalte) plastic waste, Egypt. J. Chem. 64 (2021) 773–780. https://doi.org/10.21608/EJCHEM.2020.4555 4.2928.

[42] J. Cenens, R.A. Schoonheydt, VISIBLE SPECTROSCOPY OF METHYLENE BLUE ON HECTORITE, LAPONITE B, AND BARASYM IN AQUEOUS SUSPENSION., Clays Clay Miner. 36 (1988) 214–224. https://doi.org/10.1346/CCMN.1988.0360302.

[43] M. Taj Muhammad, M.N. Khan, Study of electrolytic effect on the interaction between anionic surfactant and methylene blue using spectrophotometric and conductivity methods, J. Mol. Liq. 234 (2017) 309–314. https://doi.org/10.1016/j.molliq.2017.03.102.

[44] M. Lee, P. Cooper, Alkyl dimethyl benzyl ammonium chloride adsorption mechanism on wood, Cellul. J. 17 (2010) 1127–1135. https://doi.org/10.1007/s10570-010-9447-1.

[45] F. Bukiet, G. Couderc, J. Camps, H. Tassery, F. Cuisinier, Wetting properties and critical micellar concentration of benzalkonium chloride mixed in sodium hypochlorite, J. Endod. 38 (2012) 1525–1529. https://doi.org/10.1016/j.joen.2012.07.008 S0099-2399(12)00732-7 [pii].

[46] J.T. Davies, Reprinted from : Gas/Liquid and Liquid/Liquid Interfaces. Proceedings of 2nd International Congress Surface Activity, Butterworths, London, 1957. http://www.firp.ula.ve/archivos/historicos/57 _Chap_Davies.pdf.

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[47]   R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, Environmental organic chemistry, 2nd ed., A JOHN WILEY & SONS, INC., New Jersey, 2003. https://doi.org/10.1002/0471649643.

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