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Micellization Properties, Molal Volume and Polarizability of Newly Synthesized Gemini-Cationic Surfactants

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Abstract

In the present study, three Gemini cationic surfactants were prepared and characterized: N,N′-((1,4-phenylenebis(oxy))bis(2-oxoethane-2,1-diyl))bis(N,N-dimethyl-3-octanamidopropan-1-aminium) (C1), N,N′-((1,4-phenylenebis(oxy))bis(2-oxoethane-2,1-diyl))bis(3-dodecaneamido-N,N-dimethylpropan-1-aminium) (C2),N,N′-((1,4-phenylenebis(oxy))bis(2-oxoethane-2,1-diyl)) bis(N,N-dimethyl-3-palmitamidopropan-1-aminiccum)(C3). In water solutions, the CMC value of the prepared surfactants was detected by conductivity, surface tension, refractive index, molal volume, and spectrophotometric measurements. The effect of mixing of Gemini surfactant on CMC value was studied and discussed. Some surface properties of surfactants like excess surface concentration and minimum area per molecule were also calculated and discussed. Solvation thermodynamic parameters such as association constant, molal volume, and polarizability were also determined and discussed. The CMC value decreased from C1 to C3 due to an increase in the carbon chain length. Different physical methods show good agreement between CMC values detected by several techniques effect of mixing surfactants on CMC was also studied For example detecting CMC value for C_1 when C_2 and C_3 are added at two concentrations, before and after the CMC values of the added surfactants, (0.00001M, 0.0003M) in water solution. and so on.

Keywords:CMC; Gemini-surfactant; Micellization; Molal volume; mixed surfactant.

1. Introduction

Surfactants, in general, have an important role in the industrial field such as food processing, oil recovery, pharmaceuticalfield,andcorrosioninhibitor[1-6].Gemini surfactant is a special type of surfactant that contains two polar parts, its looks like two surfactants attached to each other by a spacer[7,8].Gemini surfactants have a special self-assembling ability, a large number of carbon atoms in the hydrophobic part that helps in decreasing the critical micelles concentration (CMC)[9]. A Gemini surfactant has a low CMC value, high surface activity, low Kraft temperature, unusual rheological properties, multifarious aggregate structures, better wetting ability, and so on. Such unique properties,

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make Gemini surfactant like a bright diamond between other surfactants types[10,11]. The chemical nature and of the spacer are significant features affecting the morphology and size of aggregates formed in the solution. aggregation properties of Gemini molecules with amide groups strongly depend on the position and number of the amide groups.Micelle aggregation number increases with the number of amide groups in Gemini moleculethe aggregation number is primarily controlled by the length and the nature of the spacer and by the length of the alkyl chains. Gemini surfactants with short spacers (s = 2, 3, 4 methylene groups), in contrast to conventional surfactants, are capable offorming elongated, cylindrical micelles in water without any additivesalso worm-like micelles, many types of nano-aggregates of Geminis have been observed: for example, vesicles, ring shapes,nanotubes, and planar bilayers.confirmed that even slight differences in structure lead to different self-assembly behavior[12,13].

Due to these impressive properties, Gemini surfactants are used in many industrial fields; some of these materials are used to inhibit microbial growth in oil and gas fields because they can penetrate bacterial communities [14] and thus stop their growth and reproduction and have the ability to reduce the corrosion rate by adsorped on the surface of corrosion where it contains hetero atoms which having free electrons can transfer to vacant orbital in the metal, etc[15,16]

At first, surfactants are found in the monomer state in the solution organize themselves on the interface of the solution by concentration increase the amphiphilic character of the molecules begins to cause the association to larger particles called premicellar structures as (dimer -trimers and other small aggregations), forming larger aggregations called micelles this happen at concentration called critical micelle concentration (CMC).CMC is a characteristic property for each surfactant at a certain temperature, pressure and in a certain solvent, and so on [17]

Critical micelle concentration can be determined by conductivity, surface tension, spectrophotometry measurements[18], refractive index measurements[19], ion activity, dye incorporation, counterion magnetic resonance.Solvation properties for some Gemini cationic surfactants were studied, CMC value was calculated by different physical methods[20],other physicals thermodynamic properties were investigated such as density to calculate molal volume, ionic association, and polarizability. Also, refractive index, and UV spectra measurements of solutions are used to study the solvation properties [21,24]

This work aims to synthesize and characterize some of Gemini cationic surfactants, determine their CMC value using some of the physical methods such as conductivity, surface tension, refractive index, molal volume, and UV spectroscopy. Some of the surfactant's solvation properties were also studied.

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2. Experimental

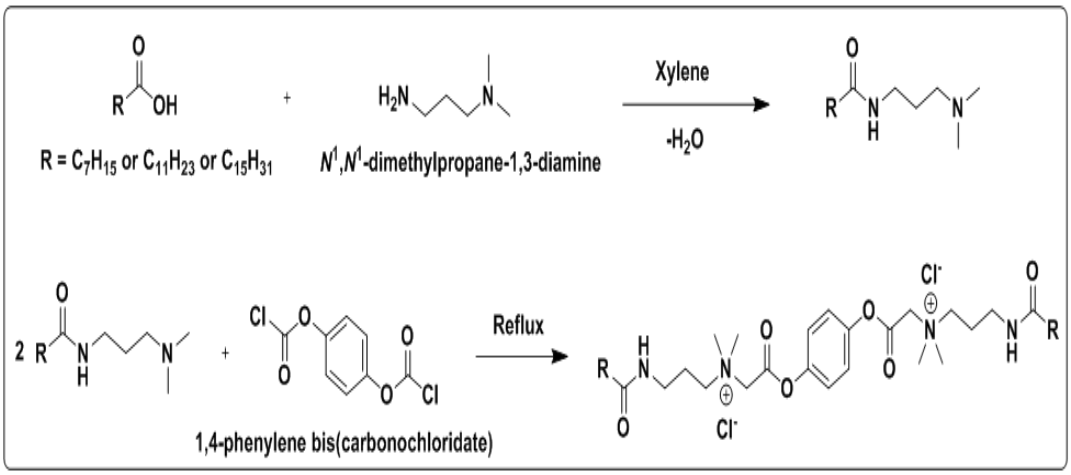
The general procedures for the synthesis of Gemini

cationic surfactants were represented in Scheme 1 and their chemical structures are represented in structure 1.

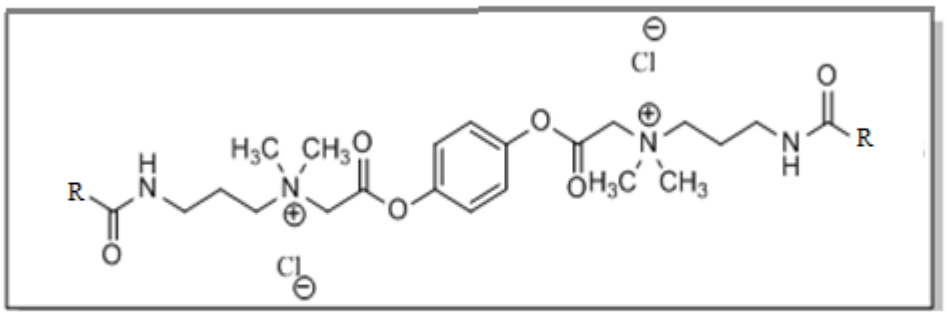
Equimolar quantities (0.15 M) of N1, N1-dimethylpropane-1,3-diamine, and fatty acid (octanoic acid, dodecanoic acid, or palmitic acid) were dissolved in 100 ml xylene (pH= 6.5) placed in 250 ml round bottom flask. P-toluene sulphonic acid (0.01%) was added to the mixture as a catalyst. The reaction mixture was refluxed for 24 h using Dean-Stark apparatus with continuous stirring. The reaction was completed after the release of (0.15 mol, 2.7 ml) water. Diethyl ether (25 ml) was added to a cold solution and stirred to get rid of the catalyst. A separating funnel was then used to separate the solvents and the desired product.

2.2. Synthesis of quaternary ammonium salt

Under the nitrogen atmosphere, the 1,4-phenylene bis (carbonochloridate) (0.1 mol) was added slowly to the reactor containing the prepared alkyl amide derivatives (0.2 mol) in100ml ethyl alcohol(pH=7.3), total quality 1 wt% sodium hydroxide as the catalyst, the reaction mixture was refluxed for 48 h at 70 °C. A precipitate was isolated by vacuum distillation for the solution and recrystallized three times using diethyl ether solvent (25 ml). The obtained Gemini cationic surfactants from octanoic acid, dodecanoic acid, and palmitic acid were coded as C1, C2, and C3 respectively.[23]



Scheme. 1. General scheme for the synthesis of Gemini cationic surfactants



R= C_7H_{15} or $C_{11}H_{23}$ and $C_{15}H_{23}$ for C1-C3 respectively

Structure .1.Chemical structure for C1.For C2 and C3 replace (C_7H_{15}) with ($C_{11}H_{23}$) and ($C_{15}H_{23}$) respectively.

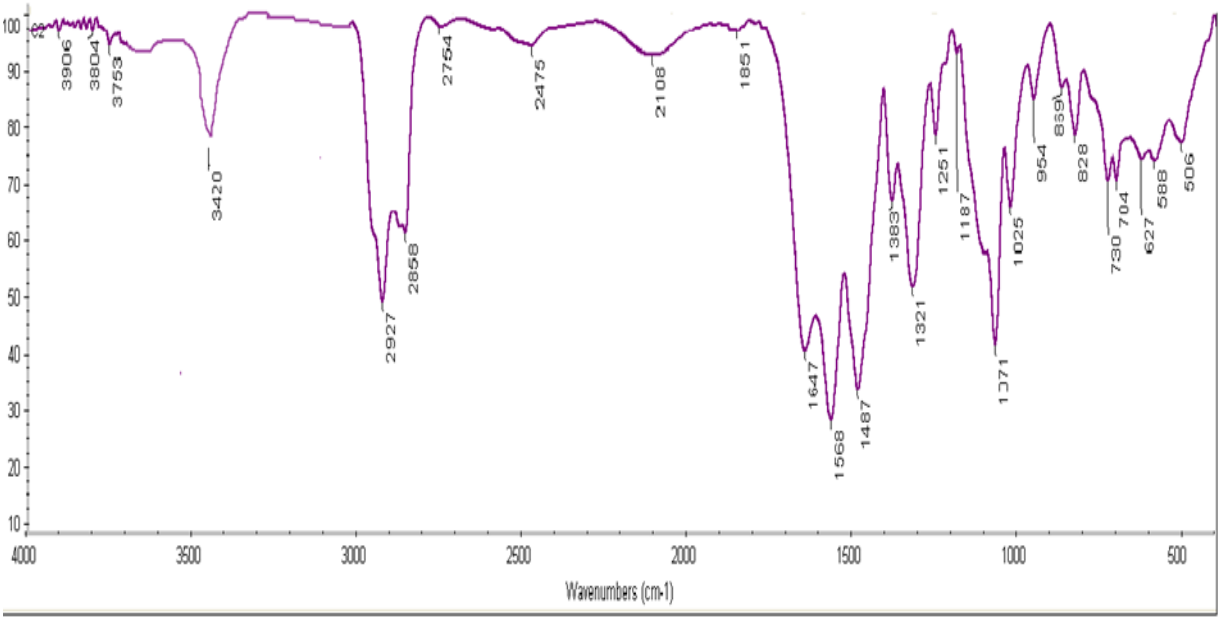


Fig. 1. FTIR chart of C3 surfactant

2.3. Apparatus and procedure

The procedure and the apparatuses that were used in this paper were reported previously [13]. CMC values in water solution at 298K for three newly synthesized Gemini cationic surfactants were detected by several techniques such as conductivityusing a Jenway Conductivity Bridge of certainty (± 0.025 µS cm−1)type (MLW 3230, Germany), refractive index using (Digital Refractometer- DR101-60- A. KRÜSS Optronic GmbH – Germany), surface tension using Kruss K9, UV measurements using UV-Visible double beam Spectroscopy Model:Jasco V-630.

3.1. Structure confirmation of synthesized Gemini cationic surfactants

The FTIR analysis was used to confirm the structure of the synthesized cationic surfactants through the appearance of some characteristic peaks of product functional groups and the disappearance of some functional groups for the reactants. The FTIR chart of C3 surfactant is given in Figure 1 as a representative example since the characteristic peaks and the functional groups of all the prepared surfactants are the same. The significant peaks of secondary amines appear combined with those assigned for carboxyl group to confirm the amidation amide group from a reaction between fatty acid and an amine group. The peaks located at 2850, 2920, 3277, and 1550 cm−1 are assigned for the presence of symmetric and asymmetric aliphatic C–H, −NH, and aromatic double bond of the benzene ring, respectively.

The 1HNMR analysis also used to specify the number and distribution of protons in the synthesized surfactants. Fig. 2 illustrates the 1HNMR spectrum of the C3 as representative example. There is a noticeable proton shift at: δ = 0.88 (t, 6H, –CH3) terminal methyl groups; δ = 1.26 (m, 36H, −(CH2)18) repeated methylene groups; δ = 1.55 (m, 4H, –CH2(CH2)24(CH3)¬2); δ = 1.90 (m, 4H, NH–CH2CH2CH2N(CH3)¬2); δ = 2.15 (t, 4H, −CH2C(O)NH); δ = 2.96 (s, 16H, −CH2N⊕(CH3)2 CH2–); δ = 3.35 (t, 4H,–CH2NH); δ = 7.25 (m, 4H, –Ph) aromatic protons; δ = 7.70 (s, 2H, HN–) amide protons. Some signals are slightly shifted due to the resonance effect of the benzene ring and the carbonyl groups

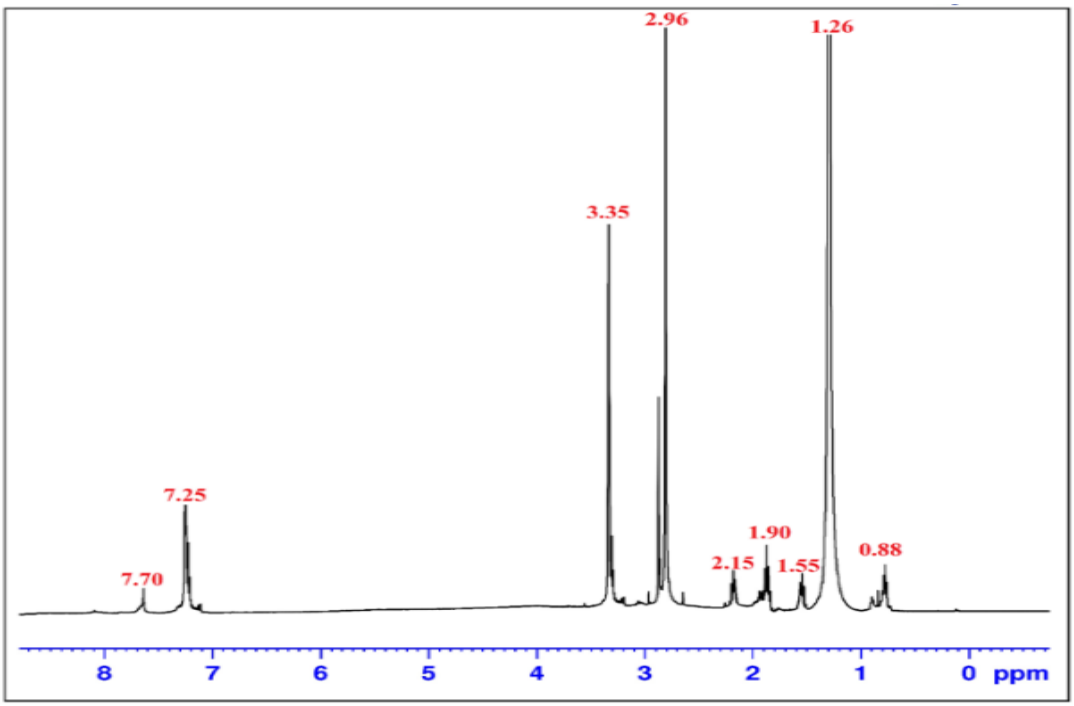


Fig.2. 1HNMR chart of C_3 surfactant.

3.2. Critical micelle concentration detection:

CMC values in water solution at 298K for three newly synthesized Gemini cationic surfactants were detected by several techniques such as conductivityas in (Fig.3), refractive indexusing as (Fig.4),surfacetension[24]as in (Fig.5),UV measurements[25]as in (Fig.6), and molal volume [28,29](Fig. 7). usingthe conductivity method, the square root of the concentration was plotted against molar conductance (∧).

In refractive index, surface tension, and molal volume methods, concentration was plotted against its related property.

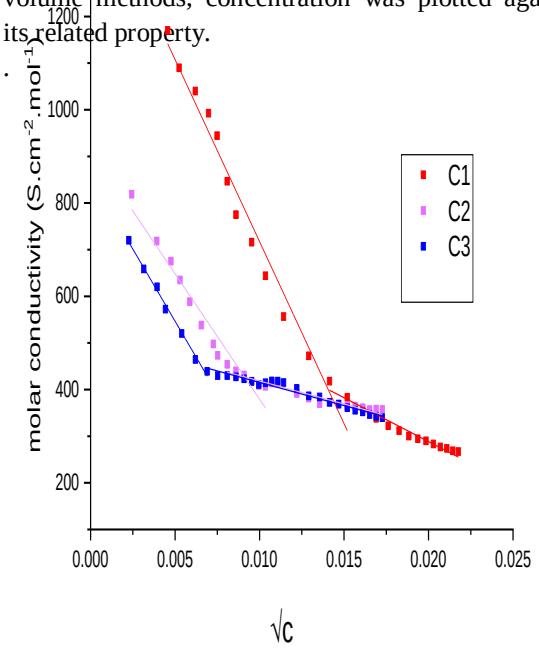


Fig.3. √c against ∧ for three newly synthesized cationic surfactants

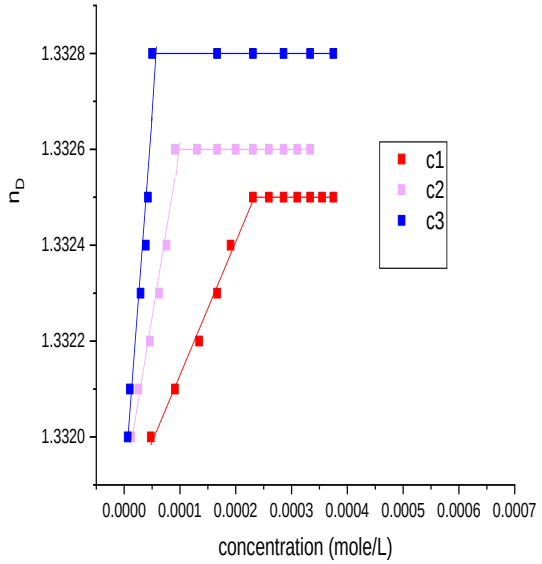


Fig.4. Concentration against the refractive index for three newly synthesized cationic surfactants.

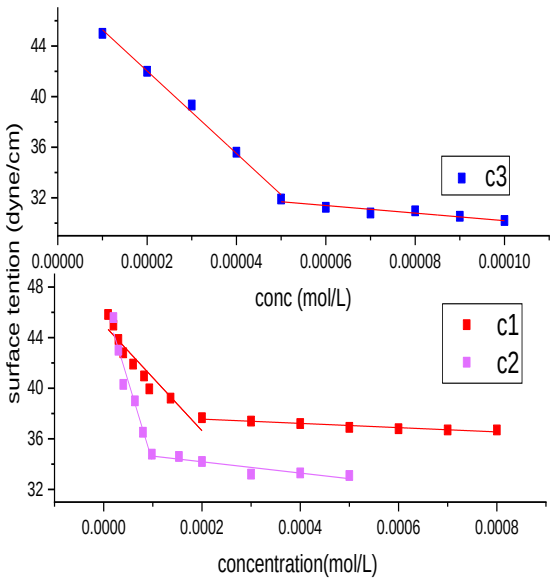


Fig.5. concentration against surface tension for three newly synthesized cationic surfactants.

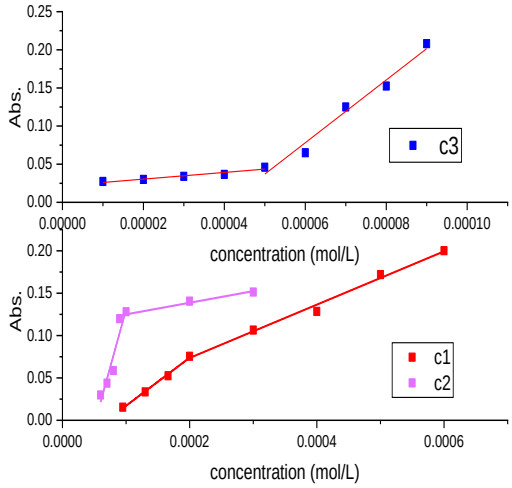


Fig6. Concentration against absorbance at the maximum wavelength for three newly synthesized cationic surfactants

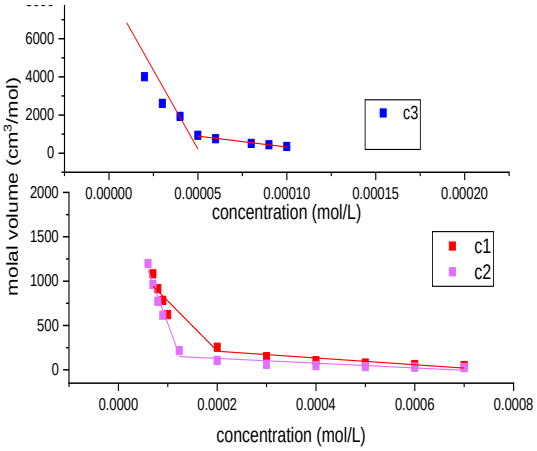


Fig.7.Concentration against molal volume for three newly synthesized cationic

Table 1: Summarized the CMC values for surfactants using different techniques.

Surfactant	CMC, mol/l				
	Conductivity	Refractive Index	Surface Tension	U.V.	Molal Volume
C1	2.01×10^{-4}	2.31×10^{-4}	1.99×10^{-4}	2.00×10^{-4}	2.03×10^{-4}
C2	0.91×10^{-4}	9.26×10^{-4}	1.00×10^{-4}	1.00×10^{-4}	1.11×10^{-4}
C3	0.49×10^{-4}	0.52×10^{-4}	0.50×10^{-4}	0.50×10^{-4}	0.50×10^{-4}

In the conductivity technique, the molar equivalent conductance decreases by concentration increase this may be related to the organization of monomers on the interface, so there is low mobility this decrease in conductivity is continuous until reaches the CMC value where micelles stars to form. micelles formation
are in equilibrium with monomers so conductivity decreases at a small rate after CMC,values of molal volume against different concentrations are located at tables (4-6).by concentration increase density increase then molal volume decrease until reach to CMC where micellization start forming the density increase sharply and mola volume decreases sharply[28]

The CMC values for surfactants understudy in water solution at 298K are represented in Table 1. Shows small CMC values as Gemini surfactants are characterized by low CMC[29]due to their high molecular weight and a high number of carbons in the hydrophobic tail. Table1and Figs. (3-7) show that the CMC value decreased by an increase in the number of carbon atoms where the increase in hydrophobic part chain length helps to form micelles at lower concentrations and so the CMC value decreased [30].a good agreement was achieved for

CMC values that were detected from different physical techniques

3.2. Thermodynamic parameters, calculated from conductivity at different concentrations:

Firstly, the standard free energy of micellization was calculated using the following equation[31].

$$\Delta G\text{mic} = (2 - \alpha)\, RT \ln [\text{CMC}] \quad (1)$$

Where α is the degree of ionization. Using the degree of ionization (α). the counterion binding parameter, β was estimated. α andβ were estimated using the following equations[34,35].

$$\alpha = {}^{S_2}/_{S_1} \quad (2)$$

$$\beta = (1 - \alpha) \quad (3)$$

Where $S_2 \,/\, S_1$ is the ratio between the slope of post- and pre-micelle regions the values of the degree of ionization, α, the counterion binding, β, and the standard free energy of micellization for the three newly synthesized cationic surfactants are reported in Table 2.

3.3. Association constant calculations

The molar conductance, Λ for surfactants understudy in water solution has been calculated from conductivity measurements, and the limiting molar, conductance, Λ^o is determined from the intercept of the relation between √C and Λ[34].

$$\Lambda = \frac{1000 \times K_S}{C} \quad (4)$$

$$\Lambda = \Lambda_0 - B\sqrt{C} \quad (5)$$

The molar conductance, Λ, and the limiting molar conductance, Λ^o values were used to calculate the association constant according to the Shedlovsky equation[35]

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} + \frac{K_a\, C \Lambda S(z) \gamma_i{}^2}{\Lambda_0{}^2} \quad (6)$$

Where S (z) is the Shedlovsky function, which can be calculated from this equation.

$$S(z) = \left\{\frac{z}{2} + \sqrt{1 + \left(\frac{z}{2}\right)^2}\right\}^2 \quad (7)$$

Where K_a is the association constant and γ_i is the activity coefficient detected from the Debye−Huckel limiting law as modified by Robinson and Stokes. The association constant values were used to calculate the standard free energy of association $\Delta G^{\circ}a$. The values of the molar conductance (Λ), limiting molar Conductance (Λ°), the association constant (K_a), and the standard free energy change of association ($\Delta G^{\circ}a$) for the surfactants understudy in water at 298.15 K are reported in Table 2.

Table 2: the degree of ionization, α, the counterion binding, β, and the standard free energy of micellization,the limiting molar conductance (Λ°), association constant (K_a), and the standard free energy change of association (ΔGa) for the surfactants understudy in Water at 298.15 K

Surfactant	A	β	ΔG_{mic} (KJ/mol)	Λ ($S.cm^2\ mol^{-1}$)	Λ° ($\mu S.cm^2\ mol^{-1}$)	K_a ($L.mol^{-1}$)	$\Delta G^{\circ}a$ (kJ/mol)
C1	0.24206	0.7579	-26.1968	1122	1599	$21.752x10^3$	-24.761
C2	0.2248	0.7752	-28.0836	666	982.55	$25.111\ x10^3$	-25.117
C3	0.166374	0.8336	-28.6068	543	855.921	$32.610\ x10^3$	-25.76

ΔG_{mic} has a negative value and the negative value increase from C_1 to C_3. The negative value indicates to spontaneous micellization process[36], and the increase in negative values refers to that C_3 has more ability to form micelle than C_2 and C_1. Which confirms the lowest CMC value for C_3[37].

From Table 2, the association constant was found to increase from C1 to C3 where C3 has the lowest CMC value. This indicates a high micellization process and subsequently high association constant and vice versa for C1, While C2 has value in between C1 and C3. The standard free energy change of association has negative values that indicate the spontaneous nature of the association and increasing in negative value from C1 to C3 indicates more association courses at C3bthan other two surfactants [40,41]

3.4. Surface properties

In water solutions at 298K, the surface tension was measured and using the measured surface tension values, some of the surface properties were calculated such as maximum surface concentration, minimum area per molecule, and effectiveness of reduction of surface areas. The maximum surface concentration (T_{max}), describe the absorbed surfactant at the interphase between air-surfactant solutions, T_{max} was calculated by using the following equation[42,43].

$$\Gamma_{max} = -\left(\frac{1}{2.303RT}\right)\left(\frac{\partial\gamma}{\partial Log\ C}\right)_{max.T.P} \quad (8)$$

Where R is the universal gas constant, Γ is the absolute temperature, and (∂γ/∂log C) is the ratio between surface tension values at CMC to concentration at CMC.The minimum area per molecule adsorbed at the interphase between air and surfactant solution is calculated using the following equation.

$$A_{min=\frac{1}{N\Gamma max}} \quad (9)$$

Where N is Avogadro number. And the effective surface tension reduction is calculated from the following equation.

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad (10)$$

Where γ_0 is the surface tension of water and $\gamma_{CMC}$is the surface tension at CMC. The surface properties were located in Table 3.

Table 3: The surface properties of the surfactants understudy.

Surfactant	π_{CMC} dyne/cm	Γ_{max} x10^3 Mol/cm^2	A_{min} x10^7 nm^2/molecule
C_1	24.32	1.785	0.9306
C_2	27.40	1.508	1.1010
C_3	30.20	1.296	1.2960

The surface properties data show that the effective surface tension reduction π_{CMC} and minimum surface area (A_{min}) are increasing by the number of carbon atoms increase. This may be related to the increase in the adsorption of the surfactant $C3 > C2 > C1$ at the air–water interface where C3 has the lowest CMC value, surfactants orient themselves away from the water, leading to a decrease in maximum surface excess concentration. This indicates an increase in the efficiency of reducing the surface tension solution of the surfactant with an increase in the hydrocarbon chain length[44,45].

3.5. Molal volume

The molal volume of surfactants understudy was determinedin water solution at 298K, using the density at molal concentration, according to the following equation[22,29]

$$V_\varphi = \frac{M}{\rho} - \frac{1000}{m}\left[\frac{1}{\rho_0} - \frac{1}{\rho}\right] \quad (11)$$

Where V_φ is the molal volume, M is the molecular weight, ρ is the density of surfactant at molal concentration, ρ_0 is the density of water, m is the molal concentration van Der Waals volume V_w, was calculated by using packing density *P,* where *P is a* ratiobetween molal volume and Van Der Waals volume and this ratio is found to be constant at large molecules, P=0.661±0.017, so Van Der Waals can be calculated using the following equation[45]

$$P = \frac{V_w}{V_\varphi} = 0.661 \pm 0.017 \quad (12)$$

Electrostriction volume refers to the volume compressed by solvent (VE), was calculated using the following equation.

$$V_E = W_W - V_\varphi \quad (13)$$

The values of the density (ρ), molal volume (Vφ), electrostriction volume (VE), and Van Der Waals volume (Vw) for the surfactants under study are presented in Tables 4-6.

Table 4: Density (ρ), Molal Volume (Vφ), Van Der Waals Volume and electrostriction Volume (VE), and (Vw) for C1.

Conc. mole/kg	ρ g/cm^3	V_φ cm^3/mole	V_W cm^3/mole	V_E cm^3/mole
7.58x10^{-5}	0.9225	1081.45	714.84	-366.61
8.64x10^{-5}	0.9250	915.04	604.84	-310.20
9.69x10^{-5}	0.9283	782.36	517.14	-265.22
10.68 x10^{-5}	0.9360	621.96	411.11	-210.84
21.15x10^{-5}	0.9473	254.72	168.37	-86.35
31.45x10^{-5}	0.9538	148.34	98.05	-50.29
41.79x10^{-5}	0.9573	102.67	67.86	-34.80
52.06x10^{-5}	0.9607	75.47	49.88	-25.58
62.33x10^{-5}	0.9629	59.28	39.18	-20.09
72.56x10^{-5}	0.9651	47.85	31.62	-16.22

Table 5: Density (ρ), Molal Volume (Vφ), Electrostriction Volume (V_E), and Van Der Waals Volume (V_w) for C_2.

Conc. mole/kg	ρ g/cm^3	V_φ cm^3/ mole	V_W cm^3/mole	V_E cm^3/mole
6.47x10^{-5}	0.9264	1197.84	791.77	-406.06
7.54x10^{-5}	0.9279	961.89	635.80	-326.08
8.54x10^{-5}	0.9364	772.42	510.56	-261.85
9.54x10^{-5}	0.9462	612.12	404.61	-207.50
10.56x10^{-5}	0.9684	215.94	142.74	-73.22
21.06x10^{-5}	0.9667	111.93	73.98	-37.95
31.35x10^{-5}	0.9791	62.192	41.11	-21.08
41.71x10^{-5}	0.9796	45.966	30.38	-15.58
51.92x10^{-5}	0.9801	36.00	23.79	-12.20
62.15x10^{-5}	0.9804	29.788	19.68	-10.09
72.36x10^{-5}	0.9807	25.274	16.70611	-8.57

Table 6: Density (ρ), Molal Volume (Vφ), Electrostriction volume(VE), and Van Der Waals Volume (Vw) for C3.

Conc. mole/kg	ρ g/cm3	Vϕ cm3/ mole	VW cm3/mole	VE cm3/mole
$1.06x10^{-5}$	0.9187	8160.81	5394.10	-2766.74
$2.13\ x10^{-5}$	0.9200	4006.05	2647.99	-1358.05
$3.18\ x10^{-5}$	0.9217	2609.44	1724.83	-884.60
$4.24\ x10^{-5}$	0.9247	1929.60	1275.46	-654.13
$5.25\ x10^{-5}$	0.9515	932.85	616.61	-316.23
$6.29\ x10^{-5}$	0.9529	754.16	498.50	-255.66
$8.35\ x10^{-5}$	0.9572	512.00	338.43	-173.57
$9.38\ x10^{-5}$	0.959	436.90	288.79	-148.11

Tables 4-6, indicate that the density of surfactants at a certain concentration, increases by molecular weight increase, then the molal volume decrease. Density, also, increases by concentration increase for three newly synthesized Gemini cationic surfactants.

3.5.1. Modeling studying for molal volume:

Molal volume was calculated for the different Gemini cationic surfactants at different concentrations at 298K. It was also modeled in terms of the following Setschenow relationship[46].

$$\text{Log } ((V\varphi)^{\circ} /(V\varphi)) = KC \qquad (14)$$

Where $(V\varphi)^{\circ}$ is the molal volume of the studied surfactants in water at the lowest concentration ($7.58x10^{-5}$,$6.47x10^{-5}$ and $1.06x10^{-5}$ for C1, C2, and C3respectively),(Vφ) is the molal volume of the studied surfactants in water at any other concentration rather than the lowest one, C is the molal concentration and K is the Setschenow constant. The Setschenow constant is a measurable parameter for the effect of concentration on the molal volume. The plots of log $((V\varphi)^{\circ} / (V\varphi))$ versus C for the surfactants understudy suggest that the following extended Setschenow equation can be applied.

$$\text{Log } ((v\varphi)^{\circ}/(V\varphi)) = K_1\, C + K_{\circ} \qquad (15)$$

The Setschenow parameters were evaluated and reported in Table 7 and shown in Figs.8.

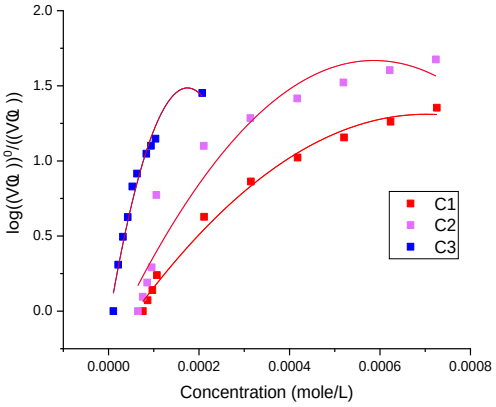


Fig.8. concentration against log $((v\varphi)^{\circ}/ (V\varphi))$ forthe three newly synthesized cationic surfactants.

Table.7. The Setschenow parameter; B_1 and R^2.

Surfactant	Model equation: $Y=\text{intercept} +B_1*x+B_2*x^2$	
	B_1	R^2
C_1	$4.461.9x10^3$	0.9883
C_2	$6.45606x10^3$	0.9333
C_3	$17x10^3$	0.96831

It was found that B_1 increases by an increase in molecular weight. For C_1, as the concentration increases the molal volume decrease ata very slow rate, while C_2 as the concentration increases the molal volume decrease ata high rate. In the case of C_3, as the concentration increases the molal volume decrease ata very high rate. This may be related to the difference in the molecular weight of the surfactants under study.

3.6. Refractive index:

For three newly synthesized Gemini cationic surfactants in water solution at 298K, at concentration $9x10^{-5}$ Molar, the molar refraction (R_m) was calculated using the following equation[47]

$$R_m = \frac{V_\varphi(n^2-1)}{n^2+2} = P_A + P_E = P_d + P_T \qquad (16)$$

Where V_φ is molal volume, n is the refractive index value at a certain concentration, p_A is the atomic polarization, P_E is the electronic polarization. P_A was calculated using the following equation.[48]

$$P_A = 1.05n^2 \qquad (17)$$

The polarizability of surfactants understudy in water solution was determined using the following equation[49].

$$\alpha = \frac{3V_{\varphi}\left(\frac{n^2-1}{n^2+2}\right)}{4N\pi} \qquad (18)$$

Where N is the Avogadro number and α is the polarizability of surfactant The values of the refractive indices, n_D, the molar refraction, R_m, the atomic polarization, P_A, and the polarizability, α, are reported in Table 8.

Table.8. the refractive index, n_D, the molar refraction, R_m, the atomic polarization, P_A, the polarizability, α of the surfactants under study.

Surfactant	n_D	R_m	P_A	α A^3x10^{23}
C_1	1.3321	160.53	1.8632	6.366
C_2	1.3326	125.78	1.8647	4.987
C_3	1.3328	89.810	1.8651	3.462

It was found that the refractive index at a certain concentration,molar refraction, and atomic polarization increase with the number of carbon chain increases this may be related to increasing micellization and solvation decrease.

3.7. Mixed surfactants

In this section, at 298Kwe study the effect of mixing surfactants on CMC values. For example detecting CMC value for C_1 when C_2 and C_3 are added at two concentrations, before and after the CMC values of the added surfactants, (0.00001M, 0.0003M) in water solution. The values of CMC for some surfactants on the presence of others using the conductivity and refractive index measurements are presented in Tables 9-11 and shown in Figs. 9-14.

Table 9: The effect of mixing surfactants C_2 and C_3 on the CMC value of C_1 using conductivity and refractive index measurements.

Adding C_2 and C_3 to C_1	CMC Value Mol/L	
	Conductivity	Refractive index
C_2(0.00001M) Before CMC	2.87x10^{-4}	2.44 x10^{-4}
C_2(0.0003M) After CMC	0.89 x10^{-4}	0.11 x10^{-4}
C_3(0.00001M) Before CMC	2.40 x10^{-4}	2.39 x10^{-4}
C_3(0.0003M) After CMC	1.319 x10^{-4}	1.61 x10^{-4}

Table 10: The effect of mixing surfactants C_1 and C_3 on the CMC value of C_2 using conductivity and refractive index measurements.

Adding C_1 and C_3 to C_2	CMC Value	
	Conductivity	Refractive index
C_1(0.00001M) Before CMC	1.79x10^{-4}	1.80 x10^{-4}
C_1(0.0003M) After CMC	0. 15 x10^{-4}	0. 12 x10^{-4}
C_3(0.00001M) Before CMC	1.432 x10^{-4}	1.51230 x10^{-4}
C_3(0.0003M) After CMC	0. 57 x10^{-4}	0. 57 x10^{-4}

Table 11: The effect of mixing surfactants C_1 and C_2 on CMC value of C_3 using conductivity and refractive index measurements.

Adding C_1 and C_2 to C_3	CMC Value	
	Conductivity	Refractive index
C1(0.00001M) Before CMC	0.70 x10^{-4}	0. 66 x10^{-4}
C1(0.0003M) After CMC	0.35x10^{-4}	0. 31 x10^{-4}
C2(0.00001M) Before CMC	0. 55x10^{-4}	0. 56x10^{-4}
C2(0.0003M) After CMC	0. 36 x10^{-4}	0. 47 x10^{-4}

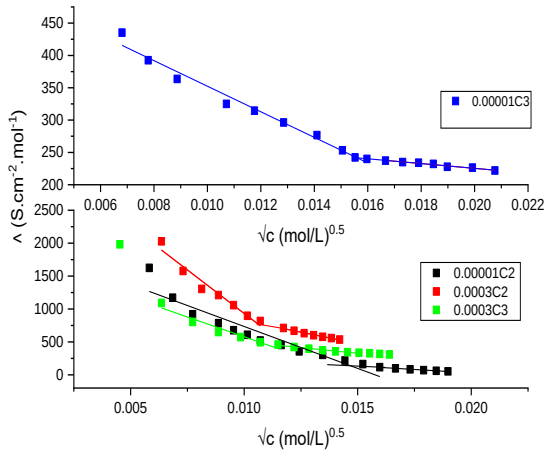


Fig.9: Effect of two different concentrations (0.00001M, 0.0003M) of $C_2$and C_3 on CMC value of C_1 using conductivity.

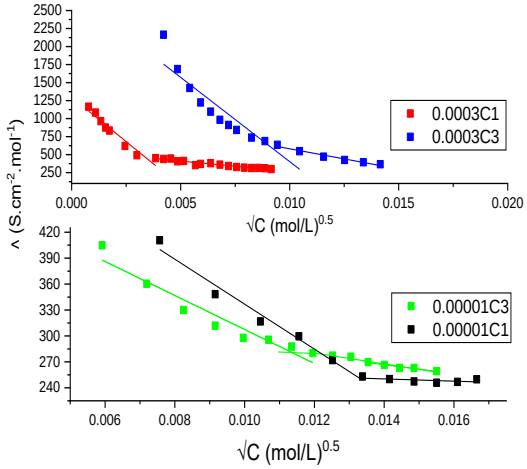


Fig.10: Effect of two different concentrations (0.00001M, 0.0003M) of C_1 and C_3 on CMC value of C_2 using conductivity.

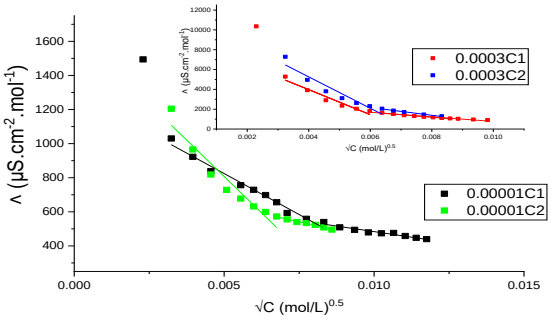


Fig.11: Effect of two different concentrations (0.00001M, 0.0003M) of C_1 and C_2 on CMC value of C_3 using conductivity.

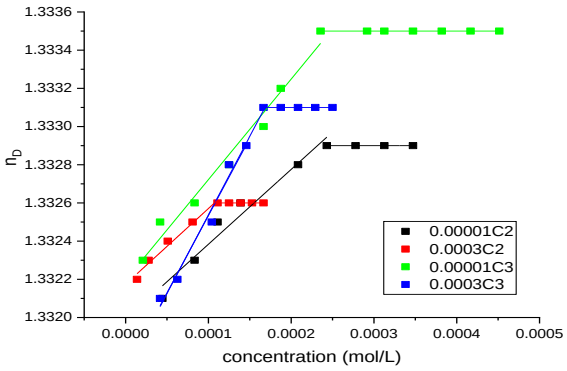


Fig.12: Effect of two different concentrations (0.00001M, 0.0003M) of $C_2$and C_3 on CMC value of C_1 using refractive index (n_D)

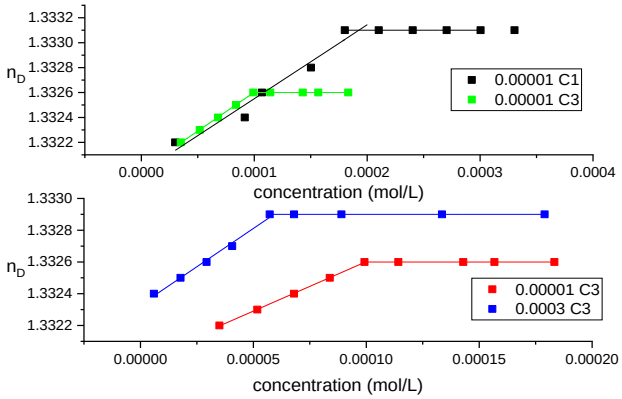


Fig 13: Effect of two different concentrations (0.00001M, 0.0003M) of $C_1$and C_3 on CMC value of C_2 using refractive index (n_D)

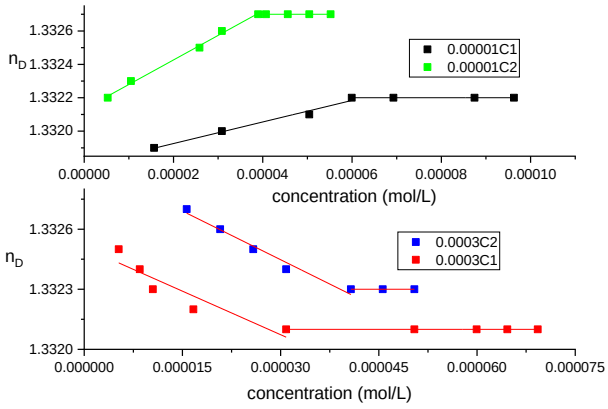


Fig.14: Effect of two different concentrations (0.00001M, 0.0003M) of C1 and C2 on CMC value of C3 using refractive index (n_D)

From the Figures (9-14) and Tables (9- 11), it was observed that the added surfactants with a concentration lower than its CMC value (0.00001M); lead to an increase in CMC value for three surfactants. This may be related to the competitionbetween surfactants. On the other hand, when added surfactant at a concentration higher than its CMC value (0.0003M), CMC value was decreased for all three surfactants. This may be due to the synergistic effect where two polar head groups and two hydrophobic chains relocate themselves simultaneously from the aqueous to micellar phase The hydrophilicity of the spacer also might be a reason for the micelle formation at a much lower concentration.concentration increase, Gemini surfactant possessing higher hydrophobicity micellization become easier, and critical micelle concentration decrease [51,52]

3.8. UV-Visible spectra

UV-Visible spectra for the surfactants understudied at concentration 0.001M at 298K, in ethanol-water mixed solvents with different percentages of ethanol (30%-50%-70%-90%) are represented in Figs. 16-18. Table.12 represents the absorbance at maximum wavelength.

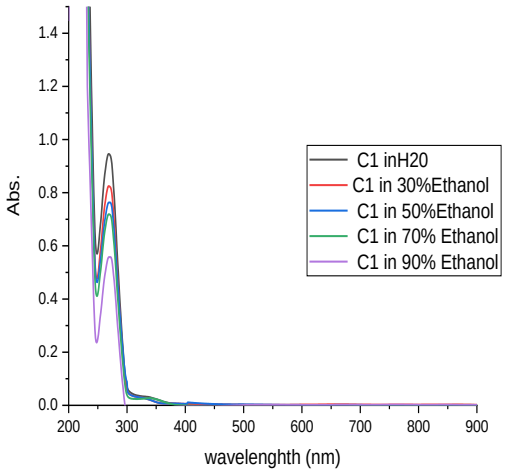


Fig.15. UV-Visible spectra of C1 (0.001 M) in the ethanol−water mixed solvent with different percentages of ethanol.

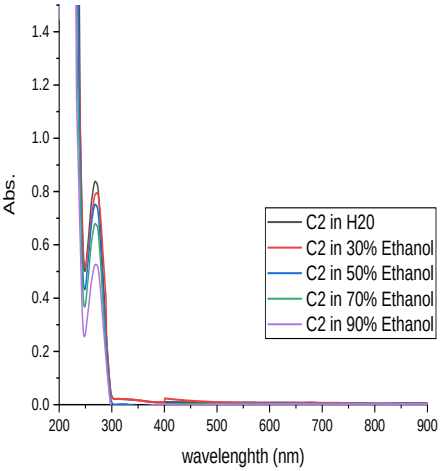


Fig.16. UV-Visible spectra of C2 (0.001 M) in the ethanol−water mixed solvent with different percentages of ethanol.

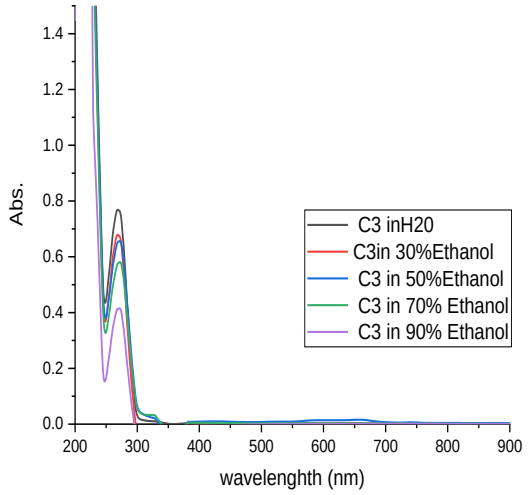


Fig.17. UV-Visible spectra of C_3 (0.001 M) in the ethanol−water mixed solvent with different percentages of ethanol.

Table 12. Absorbance and Wavelength (λ) of Surfactants at 298.15 K in the ethanol−water mixed solvent with different percentages of ethanol

Surfactant	Ethanol %	Wavelength (nm)	Absorbance
C_1	0	272	0.9450
	30	268	0.8241
	50	268	0.7617
	70	268	0.7181
	90	268	0.5570
C_2	0	272	0.8372
	30	268	0.7947
	50	268	0.7518
	70	268	0.6790
	90	268	0.5248
C_3	0	272	0.7684
	30	268	0.6790
	50	268	0.6564
	70	272	0.5808
	90	268	0.4127

The results of the UV-Visible spectra show a hypochromic effect (decrease in absorption at a certain wavelength). This may be due to a change in the dielectric properties of the solvent, and the disruption of the hydrogen bonds as a result of the interaction with ethanol than that with water molecules[52]

4. Conclusions

In this study, three Gemini cationic surfactants were synthesized and characterized using FTIR and 1HNMR. These surfactants have an important role in the industrial field where surfactants are widely used in drugs, emulsifiers, wetting agents, and so on. its characterized by low CMC. Critical micelle concentration was detected for the newly syntheses surfactant using different physical methods such as conductivity, refractive index, molaL volume, surface tension, and UV measurements. agood agreement between different methods was achieved. A decrease in CMC and an increase in a negative value of ΔG_{mis}were found by the increase in the number of carbon atoms. Also, an increase in association constant and a negative value of ΔG_a. was found by molecular weight increase. Other thermodynamic parameters were calculated and the effect of mixed surfactant on CMC was studied and discussed.

5. References

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