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Thermodynamic parameters and surface active properties for some novel polymeric cationic and nonionic surfactants

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Abstract

Two different types of polymeric surfactants (nonionic and cationic) were prepared based on homopolymerization of triethanolamine acrylate monomer. Triethanolamine acrylate monomer obtained by esterification of acrylic acid with triethanolamine and polymerized giving compound named (PTEAA). The nonionic polymeric surfactants named (PTEAAN.10 and PTEAAN.12) were prepared by esterification of PTEAA with Decanoic acid and Lauric acid. The cationic polymeric surfactants named (PTEAAC.10 and PTEAAC.12) were prepared by quaternization of PTEAA with 1-bromodecane and 1-bromododecane. The structure was confirmed by FTIR, ^{1}H-NMR, ^{13}C-NMR spectroscopic data, and GPC. The surface tension of the aqueous solution by these surfactants was measured at different temperatures. The critical micelle concentration (CMC), effectiveness ($\boldsymbol{\pi_{cmc}}$) , minimum surface area ($\mathbf{A_{min}}$), and maximum surface excess ($\boldsymbol{\Gamma_{max}}$) were calculated. The surface activity measurements showed their high affinity towards adsorption, micellization and their good surface tension reduction. The thermodynamic parameters of micellization ($\Delta \mathbf{G}^{\circ}_{\mathbf{mic}}$,$\Delta H^{\circ}_{mic}$,$\Delta S^{\circ}_{mic}$) and adsorption ($\Delta \mathbf{G}^{\circ}_{\mathbf{ads}}$,$\Delta H^{\circ}_{ads}$,$\Delta S^{\circ}_{ads}$) showed their tendency towards adsorption at the interfaces and also micellization in the bulk of their solutions. The obtained data give the opportunity to use these surfactants as corrosion inhibitors in petroleum fields.

Keywords: Cationic Surfactants; Nonionic Surfactants; surface activity; adsorption free energy; thermodynamic parameters.

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1. Introduction:

Surfactants can aggregate in clusters in solutions, which is an essential process in many applications like detergent, pharmaceutical applications, designing the microemulsion, and emulsion polymerization. Besides that, the surfactants can adsorb on the interfaces, which is a crucial process in different applications like corrosion inhibitors, bactericides, emulsifiers, and enhancing oil recovery [3-5].

Micellization character is the reason why surfactants are widely used in biology, pharmaceuticals, and chemistry. So micelle formation became a hot topic of interest [6].

For polymeric cationic surfactants,

They can self-assemble in supermolecular assemblies such as micelles. These formed assemblies create a sharp polarity gradient at the interface and define clear hydrophobic (lipophilic) regions in an aqueous solution. Those properties can have used for the design of new materials. Micellization character is affected by temperature, for instance, the hydrophobic and head group interactions change with temperature. Consequently, CMC against temperature studies gained an enormous interest to obtain information on these interfaces [7-9].

In polymeric nonionic surfactants, CMC reductions as the temperature are increased. This because of an increase in the damage of H-bonds between water molecules and surfactants hydrophilic groups. This reduction in CMCs values is lower than polymeric cationic surfactants due to the presence of Quaternary nitrogen atom [10].

The recent study objects, the first is to synthesize a new family of polymeric surfactants (nonionic and cationic) with different hydrocarbon chain lengths. The second object, our attention should be extended to investigate the surface active and thermodynamic properties of these surfactants.

2. Materials and Measurements:

2.1. Materials:

Triethanolamine (TEA) and acrylic acid (AA) were purchased from (Aldrich); 1-bromodecane, 1-bromododecane, Decanoic acid and Lauric acid were obtained from (Merck-Germany). Analytical grade solvents were used as received. Hydroquinone was used as a polymerization inhibitor at 200 ppm to prevent robust self-polymerization of AA when exposed to heat or light.

2.2. Preparation of the Two Different Types of Surfactants:

2.2.1. Preparation of 2-(bis(2-hydroxy)amino)ethyl acrylate Monomer (TEAA):

Triethanolamine (0.1 mole) was esterified with acrylic acid (0.1 mole) in the presence of xylene (solvent) and 0.01 % P-TSA (para-toluene sulfonic acid) as a catalyst and HQ (hydroquinone) as an inhibitor, until the azeotropic amount of water was collected. The prepared monoester -(2-(bis(2-hydroxy) amino) ethyl acrylate)- was purified using neutral aluminum oxide column to remove the inhibitor then dried in an oven at 55 °C. The reaction steps are presented in scheme 1 [11, 12].

2.2.2. Homo-Polymerization of (2-(bis(2-hydroxy) amino)ethyl acrylate):

The polymerization reaction was achieved in test tubes equipped with stirrers. About 2.21 g of freshly prepared monomer was introduced into the tube with a proper amount of distilled water. Initiator KPS (potassium persulphate) was added. Deoxygenation process was achieved by inserting N gas into the test tubes for twenty min., sealed and placed in H_2O bath at (70 °C/18 hrs) with dynamic stirring. After a definite reaction time, the test tubes submerged in (0 °C/ 1 h) an ice bath with continuous stirring. The result was a slightly viscous liquid that was decanted into methanol at a ratio (1:10 v/v) with agitation and was allowed to stand at room temperature overnight. After this period; the solvent decanted and the polymer was obtained which named PTEAA.

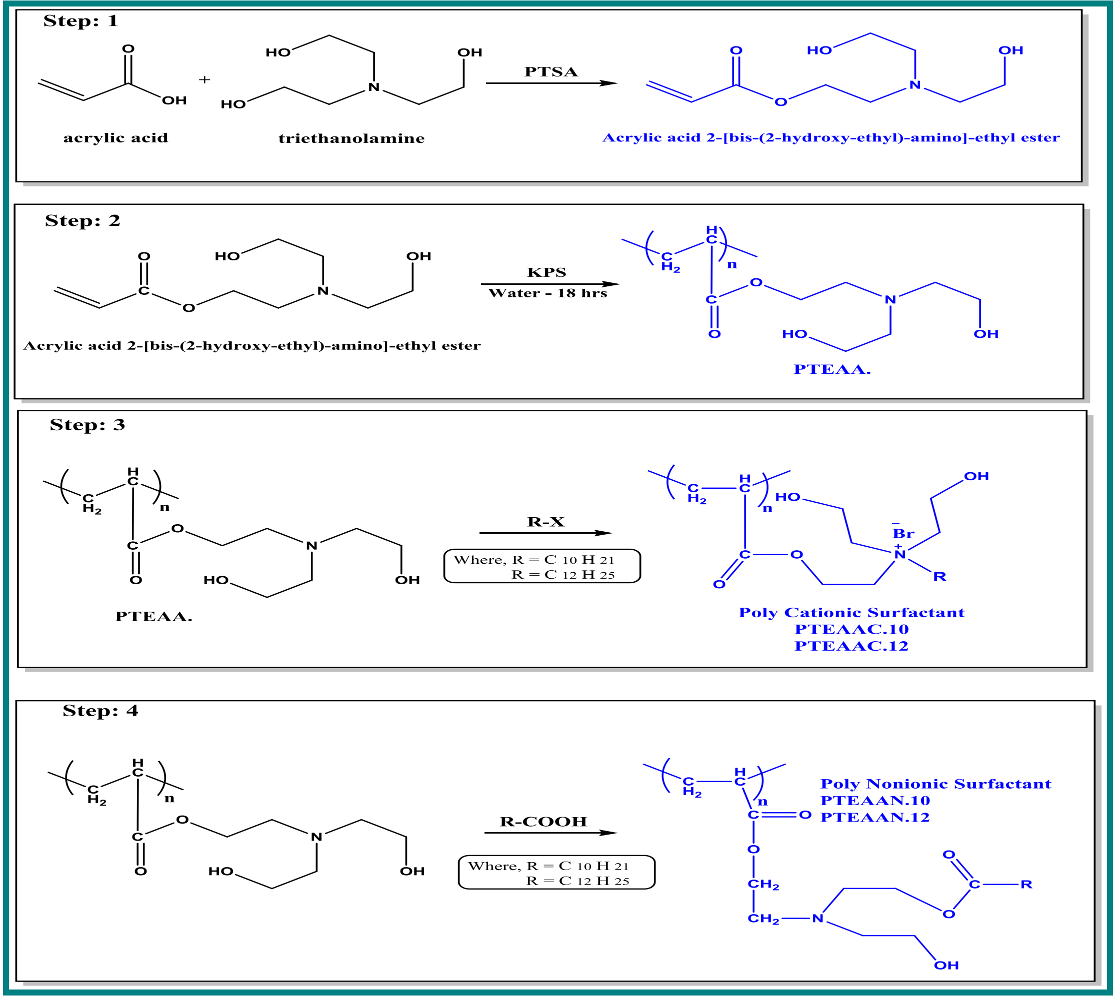
2.2.3. Quaternization of The Prepared Homo Polymer:

Quaternization reaction of 0.1 mol of the prepared polymer (PTEAA) by 0.12 mol with different alkyl Bromides (1-bromodecane and 1-bromododecane) in ethanol at 70 ºC for 48 h to produce two Polymeric cationic surfactants (PTEAAC.10 and PTEAAC.12). The reaction mixture was permitted to cool down.

2.2.4. Esterification of the Prepared Homo Polymer:

Esterification of 0.1 mol of the prepared polymer (PTEAA) by 0.12 mol with different fatty acids (Decanoic acid and Lauric acids) in DMF at 140 ºC and 0.01% P-TSA (para-toluene sulfonic acid) as a catalyst for 48 hrs., until the theoretical amount of water was collected, to produce two Polymeric nonionic surfactants (PTEAAN.10 and PTEAAN.12).

The produced polymeric surfactants were further refined by diethyl ether then recrystallized from ethanol. The steps of the reaction were illustrated in Scheme 1. The theoretical and practical M.Wt of the prepared polymeric surfactants were calculated using GPC and listed in Table1.



Scheme (1): Steps of the preparation of polymeric surfactants (PTEAA), Poly cationic surfactants (PTEAAC.10 and PTEAAC.12) and Poly nonionic surfactants (PTEAAN.10 and PTEAAN.12).

Table (1): The Expected M.Wt. and Practical M. Wt. for PTEAA, PTEAAN.10, PTEAAN.12, PTEAAC.10 and PTEAAC.12 using GPC.

Compound	Theoritical M. Wt (Monomer) (g.mol^{-1})	Theoretical M. Wt. (Polymer) (g.mol^{-1})	Practical M. Wt. (Polymer) (g.mol^{-1})
PTEAA	205.25	41,871	42,000
PTEAAN.10	371.62	75,810	45,000
PTEAAN.12	399.62	81,522	48,350
PTEAAC.10	424.49	86,595	57,240
PTEAAC.12	452.49	92,307	61,000

2.3. Surface Tension (γ) Measurement

The surface tension of different concentrations of the synthesized polymeric surfactants (cationic and nonionic) was measured via Tensiometer – Krǜss 6 processor using the ring method at 25, 35, 45 and 55 °C, the ring washed with acetone after immersed in clean water. The prepared polymeric surfactants aqueous solutions were stayed 2:3 minutes before tested. The surface tension readings were taken three times for each trial through nearly 2.5 min interval between each reading, and the values were taken as the average of these recorded values [13, 14].

2.4. Emulsion Stability:

Emulsification power of the synthesized polymeric surfactants (cationic and nonionic) was measured by robustly shaking the synthesized polycationic surfactant solutions (0.1 Wt. %, 10 ml) with 10 ml of oil (Paraffin oil) at 25 °C forming a consistent mixture in 100 ml graduated cylinder. The container was shaken strongly for 10-12 min. Then allowable to settle. The separation period for 9 ml of pure watery surfactant solution was noted. The mean of the three tests for each type of surfactant was recorded as an indication of emulsification power.

2.5. Foaming Power:

Foaming power of the synthesized polymeric surfactants (cationic and nonionic) (PTEAAC.10, PTEAAC.12, PTEAAN.10, and PTEAAN.12) was measured by well shaking of 100 mL (0.1% conc.) of the surfactant solution robustly in a tightly closed 200 mL cylinder at 25 °C. Foam height and stability ware measured in mL and sec, respectively.

3. Result and Discussion:

3.1. Confirmation the Chemical Structure of the Prepared Polymeric Surfactants:

FT-IR of the prepared compounds monomer (TEAA), Homopolymer (PTEAA), PTEAAC.12 as a representative polymeric cationic surfactant, and PTEAAN.12 as a representative polymeric nonionic surfactant was shown in Fig (1.a, b, c, and d) respectively. From Fig (1.a), which shows FT-IR Spectrum of TEAA, it can observe that, sharp peak at 1732 cm^{-1} due to the carbonyl group of the ester compound; peak at 1660 cm^{-1} due to the double bond of acrylate and broad peak at 3386 cm^{-1} for the hydroxyl group of triethanolamine. As shown in Fig (1.b), Homopolymer (PTEAA), shows the disappearance of C=C peak and shifting in ester to 1734 cm^{-1} due to Homopolymerization of the triethanolamine acrylate. FT-IR of Cationic surfactant (PTEAAC.12) shown in Fig (1.c), shows appearance of strong peak at (1072 cm^{-1}) for (N^+) with multi-broad peaks at (2050-3200 cm^{-1}), and two firm absorption peaks at 2895 cm^{-1} and 2929 cm^{-1} are due to stretching and bending vibrations of (CH_3) and (CH_2) of long alkyl chain due to quaternization reaction. Fig (1.d) shows two very strong peaks at 2843 cm^{-1} and 2919 cm^{-1} which referred to CH-aliphatic stretching vibration bands of the alkyl groups. Also overlapping and shifting at 1734 cm^{-1} due to the carbonyl group of the prepared polymeric nonionic surfactant.

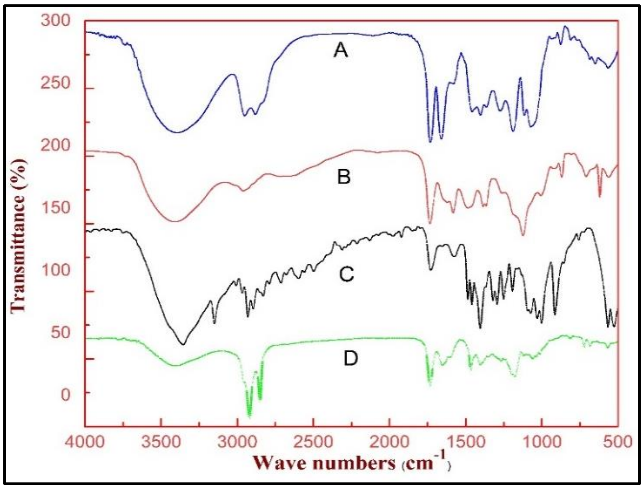


Fig (1): FTIR spectrum of (A) Monoester (TEAA). (B) Homo polymer (PTEAA). (C) Poly cationic surfactant (PTEAAC.12). and (D) poly nonionic surfactant (PTEAAN.12).

The ^{1}H-NMR and ^{13}C-NMR spectra of PTEAAC.12 in (DMSO) as a representative sample for the synthesized polycationic surfactants shown in Fig (2.a) and Fig (2.b) respectively.

Fig (2.a) showed different signals at δ = 0.98 ppm for ($N^+CH_2(CH_2)_n\underline{CH_3}$); δ = 1.2-1.3 ppm for ($N^+CH_2(\underline{CH_2})_nCH_3$); δ = 1.4 ppm for ($OCO\text{-}CH\underline{CH_2}\text{-}$); δ = 2.1 ppm for ($OCO\underline{CH}CH_2$); δ = 3.1 ppm for ($N^+\underline{CH_2}(CH_2)_nCH_3$); δ = 3.4 ppm for ($N^+\underline{CH_2}CH_2OH$); δ = 3.9 ppm for ($N^+CH_2\underline{CH_2}OH$); δ = 3.9 ppm for ($N^+\underline{CH_2}CH_2OCO$); and δ = 4.11 ppm for ($N^+CH_2\underline{CH_2}OCO$).

^{13}C-NMR (DMSO) spectrum of PTEAAC.12 represented in Fig (2.b), illustrated different signals at δ = 14.1 ppm for ($N^+CH_2CH_2(CH_2)_9CH_2\underline{CH_3}$); δ = 22 ppm for ($N^+CH_2CH_2(CH_2)_9\underline{CH_2}CH_3$); δ = 24.2 ppm for ($N^+\underline{CH_2}CH_2(CH_2)_9CH_2CH_3$); δ = 28.2 ppm for ($N^+CH_2\underline{CH_2}(CH2)_9CH_2CH_3$); δ = 29.5 ppm for ($N^+CH_2CH_2(\underline{CH_2})_9CH_2CH_3$); δ = 31.8 ppm for ($N^+CH_2CH_2(CH_2)_9\underline{CH_2}CH_3$); δ = 56 ppm for ($N^+CH_2\underline{CH_2}OH$); δ = 60,62 ppm for ($N^+\underline{CH_2CH_2}OCO$)

respectively; δ = 64 ppm for $(N^+\underline{CH_2}CH_2OH)$ and δ = 173.9 ppm for $(N^+CH_2CH_2\underline{OCO})$.

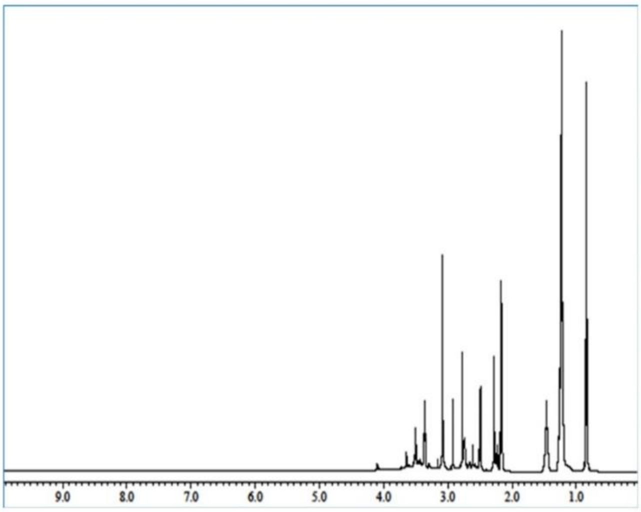


Fig (2.a): ^{1}H-NMR (DMSO) spectrum of PTEAAC.12 Poly cationic surfactant.

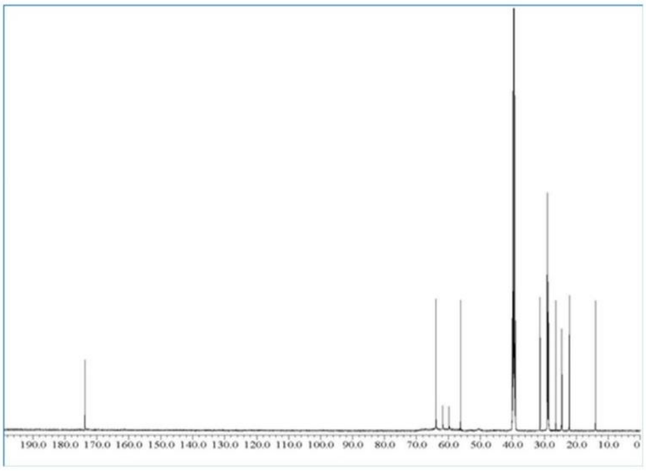


Fig (2.b): ^{13}C-NMR (DMSO) spectrum of PTEAAC.12 Poly cationic surfactant.

The ^{1}H-NMR and ^{13}C-NMR spectra of PTEAAN.12 in (DMSO) as a representative sample for the synthesized poly nonionic surfactants showed in Fig (3.a) and Fig (3.b) respectively.

Fig (3.a) showed different signals at δ = 0.85 ppm for (a, $OCOCH_2(CH_2)_n\underline{CH_3}$); δ = 1.2 - 1.3 ppm for $(OCOCH_2\underline{(CH_2)}_nCH_3)$; δ = 1.52 ppm for $(OCOCH_2(CH_3)_n\underline{CH_2}CH_3)$; δ = 2.21 ppm for $(OCOCH\underline{CH_2})$; δ = 2.43 ppm for $(NCH_2\underline{CH_2}OH)$; δ = 2.62 ppm for $(OCO\underline{CH_2}(CH_2)_nCH_3)$; δ = 2.71 ppm for $(OCO\underline{CH}CH_2)$; δ = 2.8 ppm for $(N\underline{CH_2}CH_2OH)$; δ = 3.54 ppm for $(N\underline{CH_2}CHOCO)$; δ = 4.15 ppm for $(NCH_2\underline{CH_2}OH)$; and δ = 4.45 ppm for $(NCH_2\underline{CH_2}OCO)$.

^{13}C-NMR (DMSO) spectrum of PTEAAN.12 represented in Fig (3.b), illustrated different signals at δ = 14.2 ppm for $(OCOCH_2CH_2(CH2)_9CH_2\underline{CH_3})$; δ = 20.8 ppm for $(OCOCH_2CH_2(CH2)_9\underline{CH_2}CH_3)$; δ = 22.1 ppm for $(OCO\text{-}CH\underline{CH_2}\text{-})$; δ = 24.4 ppm for $(OCOCH_2\underline{CH_2}(CH2)_9CH_2CH_3)$; δ = 29.0 – 30.5 ppm for $(OCOCH_2CH_2\underline{(CH2)_9}CH_2CH_3)$; δ = 34.0 ppm for $(OCO\underline{CH_2}CH_2(CH2)_9CH_2CH_3)$; δ = 36.4 ppm for $(OCO\text{-}\underline{CH}CH_2\text{-})$; δ = 46.3 ppm for $(N\underline{CH_2}CH_2OCO\text{-}CHCH_2\text{-})$; δ = 58.5 ppm for $(N\underline{CH_2}CH_2OH)$; δ = 58.8 ppm for $(NCH_2\underline{CH_2}OH)$; δ = 61.3 ppm for $(NCH_2\underline{CH_2}OCOCH_2(CH_2)_nCH_3)$; δ = 61.5 ppm for $(NCH_2\underline{CH_2}OCO\text{-}CHCH_2\text{-})$; δ = 172.1 ppm for $(NCH_2CH_2O\underline{CO}CH_2(CH_2)nCH_3)$; and δ = 175 ppm for $(NCH_2CH_2O\underline{CO}\text{-}CHCH_2\text{-})$.

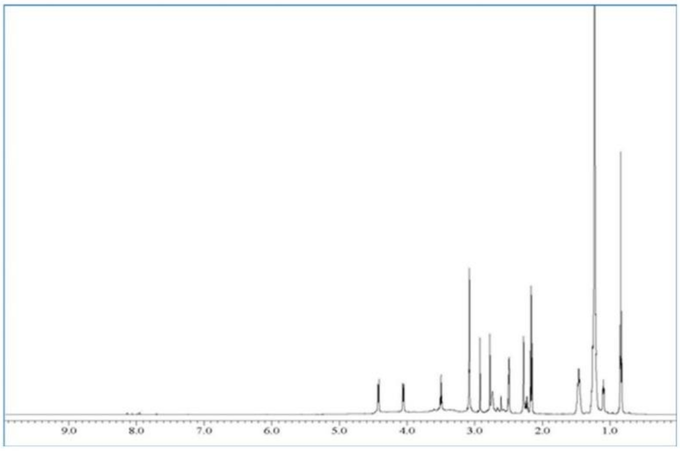


Fig (3.a): ^{1}H-NMR (DMSO) spectrum of PTEAAN.12 Poly nonionic surfactant.

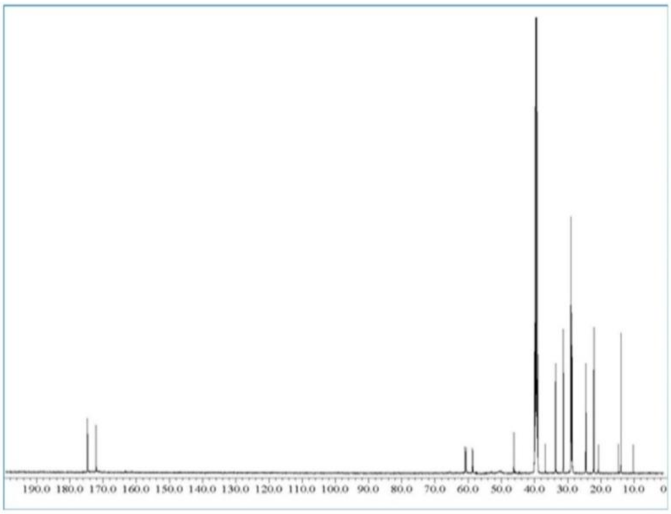
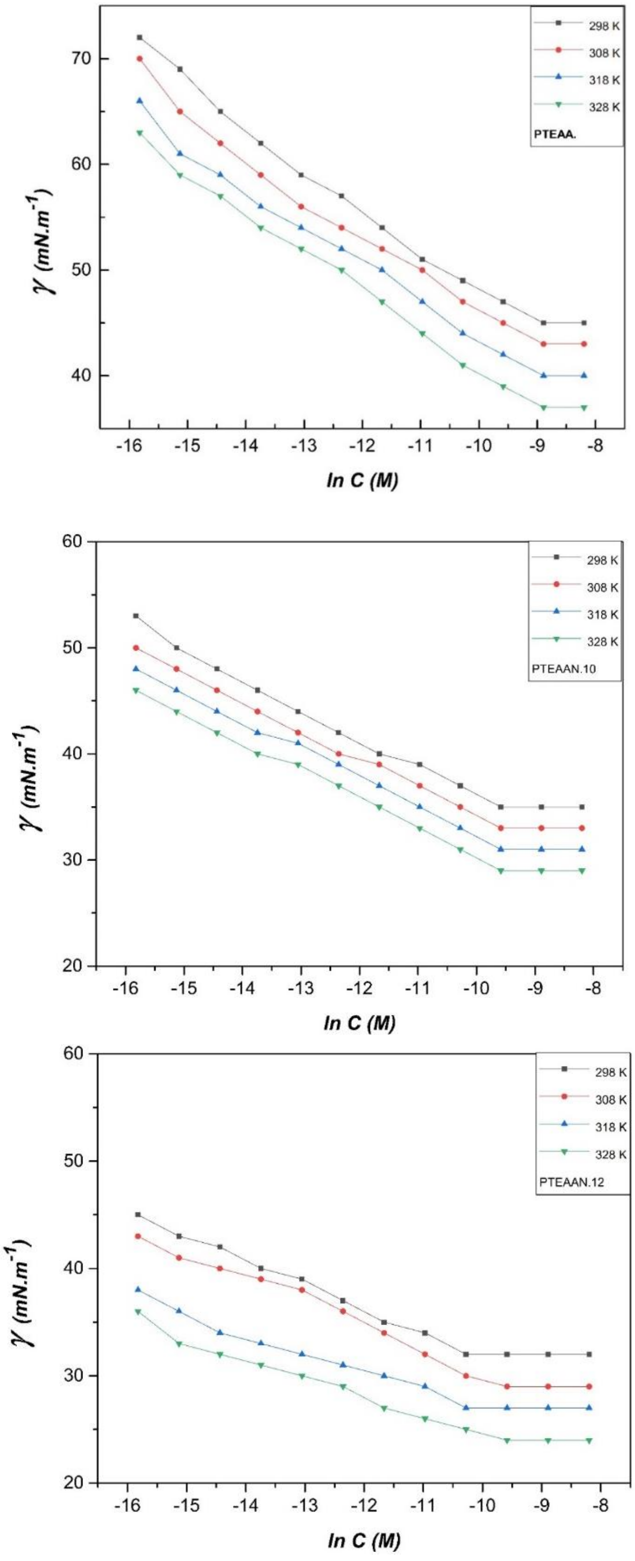


Fig (3.b): ^{13}C-NMR (DMSO) spectrum of PTEAAN.12 Poly nonionic surfactant.

3.2. Surface-active Properties:

3.2.1. Critical Micelle Concentration (CMC):

The surface tension measurements were evaluated to study the surface activity of the prepared polymeric surfactants. Fig (4) shows the surface tension plots as a function of log C for the prepared cationic and nonionic surfactants at 25, 35, 45 and 55 °C. The surface tension parameters such as (CMC, $\boldsymbol{\pi_{cmc}}$, $\boldsymbol{\Gamma_{max}}$ and $\boldsymbol{A_{min}}$) are calculated and summarized in Table 2. As shown in Table 2 and Fig (4), it can observe that, both polymeric cationic and nonionic surfactants reduce the surface tension of the water and this may be due to the good migration and adsorption on the surface which may be due to the chemical structure of the prepared surfactants. By comparing the data of surface tension, it can be observed that, the cationic surfactants reduce the surface tension more than the nonionic surfactants. The surface tension for the prepared polymeric surfactants decreases by increasing the carbon chain length, the fall in the solubility, and as a result the movement of the surfactants from the bulk to the interface can be explained by the increasing of hydrophobic moiety of the alkyl chain length.



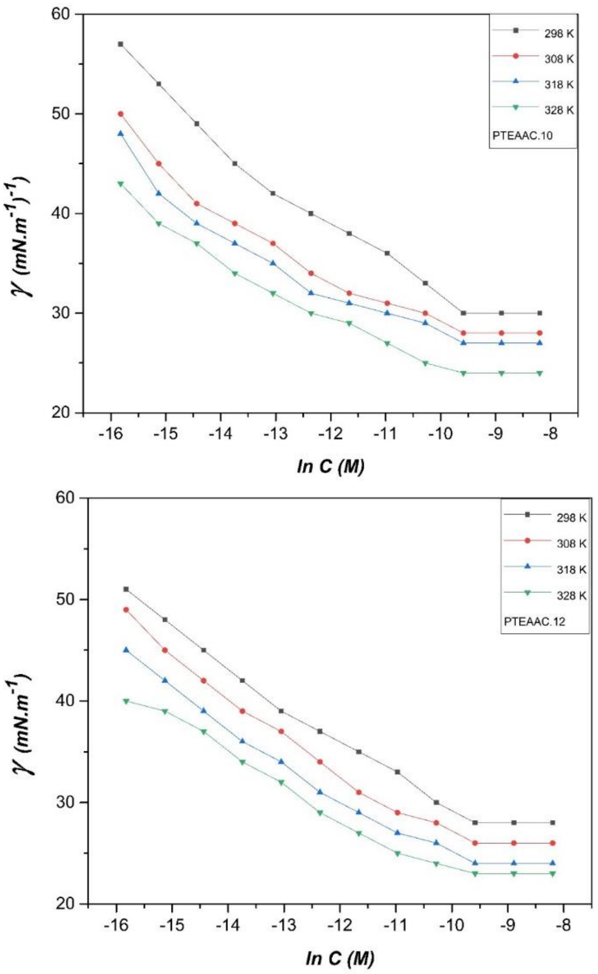


Fig (4): The relation between surface tension γ and ln C of PTEAA, PTEAAN.10, PTEAAN.12 PTEAAC.10 and PTEAAC.12 at different temperatures (°C).

The CMC of the synthesized polymeric surfactants (nonionic and cationic) was obtained through a relationship between the surface tension (γ) of the prepared polymeric surfactants against ln C in ppm at 25, 35, 45 and 55 °C. As revealed in Fig (4) and listed in Table 2, The plots of γ versus log C show a break at a concentration corresponding to the CMC of the Homopolymer and the prepared surfactants.

It can be found that the CMC values of the prepared polymeric surfactants (nonionic and cationic) less than the corresponding polymer. This can be assigned to increasing the hydrophobicity and decreasing the solubility of the prepared polymeric surfactants, therefore the free energy of system increase. This lead to the surfactant molecules aggregate into micelles, so the hydrophobic and hydrophilic groups in the prepared polymeric surfactants are oriented to the internal part of the micelle and toward the solvent, respectively. This in order to decline the contact with the aqueous solution as well as decrease the free energy of the solution. And so, as the length of the hydrophobic chain increases, the more the surfactant will tend to compromise a micelle, and therefore CMC will decrease as a result Fig (4) [3, 15].

The experimental CMC values in Table 2 and Fig (4), refer to their decreasing with elongation the hydrophobic tail for both Cationic and nonionic polymeric surfactants (PTEAAC.12 < PTEAAC.10) and (PTEAAN.12 < PTEAAN.10). The CMC is affected by the length of the hydrocarbon chain. In general, the hydrophobicity of the polymeric surfactants can be raised through the increase in the length of the hydrocarbon chain. Therefore, the increase in the hydrocarbon chain length of the polymeric surfactants leads to more aggregation and thus CMC of the solution will drop as a result.

As shown in Table 2, from 25:55 °C, a decrease in CMC values and a departure of the polymeric surfactants molecules out of the aqueous solution are observed, which can be assigned to hydrogen bond cleavage.

From the obtained results it can be observed that, the CMC of cationic surfactants higher than nonionic and this due to the presence of quaternary nitrogen, which increase adsorption of surfactant molecules at the interface [16].

Table 2: Critical micelle concentration (CMC), effectiveness (γ_{cmc}), maximum surface excess (Γ_{max}) and minimum surface area (A_{min}) of PTEAA, PTEAAN.10, PTEAAN.12, PTEAAC.10 and PTEAAC.12 at different temperatures 25, 35, 45 and 55 °C.

Inhibitors	T (°C)	CMC X10^{-5} (mol/L)	$\boldsymbol{\gamma_{cmc}}$ (mN/m)	$\boldsymbol{\pi_{cmc}}$ (mN/m)	Γ_{rmax}X 10^{11} (mol/cm^2)	A_{min} X10^{-2} (nm/molecule)
PTEAA	25	6.38	44.89	27.41	1.57	1.05
	35	5.71	42.67	27.68	1.52	1.08
	45	5.38	39.78	29	1.46	1.13
	55	4.59	37.00	31.59	1.44	1.15
PTEAAN.10	25	4.44	34.89	37.41	1.13	1.46
	35	4.07	32.77	37.58	1.07	1.54
	45	3.61	30.85	37.93	1.06	1.55
	55	3.17	28.82	39.77	1.04	1.58
PTEAAN.12	25	3.59	32.00	40.3	9.28	1.78
	35	2.94	29.02	41.33	9.12	1.82
	45	2.75	27.00	41.78	7.14	2.32
	55	2.32	23.92	44.67	7.46	2.22
PTEAAC.10	25	5.18	30.18	42.12	8.43	1.96
	35	4.92	27.02	43.33	7.02	2.36
	45	3.04	27.00	41.78	6.43	2.57
	55	2.47	24.05	44.54	6.19	2.67
PTEAAC.12	25	4.03	28.16	44.14	7.46	2.22
	35	3.57	26.04	44.31	7.28	2.27
	45	3.20	24.11	44.67	7.08	2.34
	55	2.91	23.05	45.54	6.33	2.62

3.2.2. Effectiveness ($\boldsymbol{\pi_{cmc}}$) :

The efficiency of adsorption is an essential factor for foaming and emulsification. The values of surface tension (γ_{cmc}) at CMC were used to calculate the values of surface pressure (effectiveness), using the following expression [17]:

$$\pi_{cmc} = \gamma_{\circ} - \gamma_{cmc} \qquad (1)$$

where γ_{cmc} is the surface tension at CMC and $\gamma_{\circ}$ is the surface tension of pure water measured at the required temperature, which provide a view about the synthesized surfactants properties and their proposed efficiency as promising surfactants. The π_{cmc} was calculated and listed in Table 2, The most efficient prepared surfactant is this one which yields the highest decline in the surface tension at the CMC. Table 2 shows that π_{cmc} is increased due to the increase in the length hydrocarbon chain, and so the

PTEAAC.12 is the most effective polymeric surfactant, where the least CMC value could be reached, and therefore the prepared PTEAAC.12 and PTEAAN.12 with longer tail are the most effective surfactants [3].

3.2.3. Maximum Surface Excess ($\boldsymbol{\Gamma_{max}}$):

$\boldsymbol{\Gamma_{max}}$ is the concentration of surfactant molecules at the border of interface per unit area, which depends primarily on the length of the hydrophobic chain. The ($\boldsymbol{\Gamma_{max}}$) was calculated using Gibb's equation [18]:

$$\boldsymbol{\Gamma_{max}} = \frac{1}{2.303nRT}\left(\frac{d\gamma}{d\,Log\,C}\right)_T \qquad (2)$$

Where R, is the gas constant (8.314 J mol-1 K-1); T, is the absolute temperature; $\frac{d\gamma}{d\,Log\,C}$, is the slop of γ vs. $Log\ C$ profile at the point CMC; and n is the number of counter ions that originate in solution by dissociation of the polymeric surfactant and whose concentration varies at the surface when altering the bulk solution concentration [19]. The results presented in Table 2 shows that $\boldsymbol{\Gamma_{max}}$ is declined by the increase in the hydrophobic chain length of the synthesized poly cationic surfactants. This trend reveals that, the surfactant molecules are oriented to the interface, reducing the surface energy of their solutions for both polymeric surfactants (nonionic and cationic).

From Table 2, The $\boldsymbol{\Gamma_{max}}$ for the homopolymer is higher than the prepared polymeric surfactants (nonionic and cationic), moreover $\boldsymbol{\Gamma_{max}}$ for the cationic surfactants is less than that of nonionic surfactants.

3.2.4. Minimum Surface Area ($\boldsymbol{A_{min}}$):

A_{min} is “the average area occupied by each molecule adsorbed at the interface”. The minimum surface area (A_{min}) of the synthesized polymeric surfactants were calculated and presented in Table 2 using the following equation:

$$A_{min} = \frac{10^{16}}{\boldsymbol{\Gamma_{max}} \times N_A} \qquad (3)$$

where NA is Avogadro's constant (6.022X1023 mol-1) and A_{min} is in nm2. Firstly, Where A_{min} increase by increasing the (chain length) hydrophobic moiety due to decreasing $\boldsymbol{\Gamma_{max}}$ values, where by decreasing $\boldsymbol{\Gamma_{max}}$ the spaces between molecules will increase so A_{min} increases for PTEAAN.12 and PTEAAC.12 equal 178 and 222 at 25 °C respectively; this related to that the balance of forces leading to the organization of the polymeric surfactants at the surface of aqueous solutions.

Secondly, the values of $\boldsymbol{\Gamma_{max}}$ decrease with temperature increasing from 25 to 55 °C that in turn will cause a similar increase in A_{min}. This is due to the coiling of the hydrophobic chains at the interface.

3.2.5. Thermodynamics Parameters of Micellization and Adsorption ($\Delta \boldsymbol{G^{\circ}_{mic}}$ & $\Delta \boldsymbol{G^{\circ}_{ads}}$):

The thermodynamic parameters of adsorption and micellization of the synthesized polymeric surfactants were calculated according to the following equations [20]:

$$\Delta G^{\circ}_{mic} = RT\ ln\ CMC \qquad (4)$$

$$\Delta G^{\circ}_{ads} = \Delta G^{\circ}_{mic} - 0.0602\ \pi_{cmc}\ A_{min} \qquad (5)$$

$$-\Delta S^{\circ}_{mic} = \Delta G^{\circ}_{mic}/\Delta T \qquad (6)$$

$$-\Delta S^{\circ}_{ads} = \Delta G^{\circ}_{ads}/\Delta T \qquad (7)$$

$$\Delta H^{\circ}_{mic} = \Delta G^{\circ}_{mic} + T\Delta S^{\circ} \qquad (8)$$

$$\Delta H^{\circ}_{ads} = \Delta G^{\circ}_{ads} + T\Delta S^{\circ} \qquad (9)$$

Whereas ΔG°_{ads} and ΔG°_{mic} are the adsorption and micellization free energies, respectively. From Table 3 we can observe that the values of ΔG°_{mic} and ΔG°_{ads} are negative value, inferred the spontanousness of these two processes, but there are more increase in values of ΔG°_{ads} more than of ΔG°_{mic}, signifying the tendency of the molecules to be adsorbed at the interface [21]. Also ΔG°_{ads} values increase in the negative direction by increasing both hydrophobic moiety length as well as temperature, the compounds prefer adsorption at interface, and thus declining the surface which by expanding force acting against the contracting force resulting from the surface as shown in Fig (5) [4, 22].

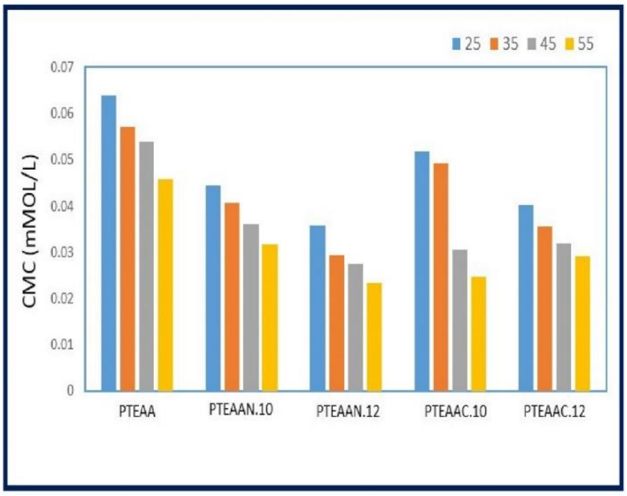


Fig (5): Temperatures & hydrophobic chain length effect of synthesized polymeric surfactant on critical micelle concentration values.

Increasing the number of polymerized PTEAA units will increase the negativity of the ΔG°_{mic} values and their micellization tendency as a result. The gradual rise in the negativity of ΔG°_{mic} matches with the sequence of the CMC values as presented in Table 3.

Table 3: Thermodynamic parameters of adsorption and micellization for PTEAA, PTEAAN.10, PTEAAN.12, PTEAAC.10 and PTEAAC.12 at different temperatures 25, 35, 45 and 55 °C.

Inhibitors	T °C	ΔG_{mic} kJ / mol^{-1}	ΔSmic KJ.mol^{-1}K^{-1}	ΔHmic Kcal.mol^{-1}	ΔG_{ads} kJ / mol^{-1}	ΔSads KJ.mol^{-1}K^{-1}	ΔHads Kcal.mol^{-1}	**ΔG_{mic}-ΔG_{ads}**
PTEAA	25	-23.93	0.069	-3.24	-25.67	0.077	-2.71	1.74
	35	-25.01		-3.63	-26.68		-2.95	1.80
	45	-25.98		-3.90	-27.62		-3.12	1.98
	55	-27.24		-4.46	-28.88		-3.61	2.19
PTEAAN.10	25	-24.83	0.091	2.29	-28.13	0.102	2.54	3.29
	35	-25.88		2.14	-29.19		2.50	3.49
	45	-27.04		1.90	-30.23		2.50	3.55
	55	-28.25		1.60	-31.46		2.29	3.78
PTEAAN.12	25	-25.35	0.085	0.21	-29.70	0.144	13.42	4.34
	35	-26.72		-0.29	-30.92		13.64	4.53
	45	-27.76		-0.47	-32.91		13.10	5.84
	55	-29.09		-0.95	-34.00		13.46	5.98
PTEAAC.10	25	-24.44	0.082	0.27	-29.48	0.167	20.47	4.99
	35	-25.40		0.15	-31.17		20.46	6.16
	45	-27.49		-1.10	-33.55		19.76	6.48
	55	-28.93		-1.71	-35.19		19.80	7.18
PTEAAC.12	25	-25.07	0.060	-6.97	-30.99	0.101	-0.84	5.91
	35	-26.22		-7.51	-32.02		-0.86	6.08
	45	-27.36		-8.05	-33.11		-0.94	6.30
	55	-28.48		-8.55	-34.87		-1.69	7.18

Also, ΔG°_{mic} increases in the negative direction by increasing the hydrophobic moiety which is higher for PTEAAN.12 and PTEAAC.12 With respect to their order [14]. Through thermodynamic parameter of adsorption and micellization, it was observed that ΔG°_{ads} are more negative than ΔG°_{mic} which implied that the molecules tend to be adsorbed at the air–water interface until the whole surface coverage. After that, the molecules will diffuse down to the solution bulk in order to form micelles [23]. Meanwhile, a slight decrease in (ΔG°_{mic}) occurred on increasing the alkyl chain length. This is due to the hydrophobic chains and their repulsion by water molecules which is the motivating factor in micelle creation. Nevertheless, the H-bonds formation and the attraction of head groups by H_2O molecules, the repulsion at the hydrophobic chain-water molecules would obey the amphiphile molecules into a fewer energetic condition which is the micelle form to lessen the previously mentioned repulsion [24].

It was found that $\Delta H°_{mic}$ acquired both positive and negative values, this revealed that the entropy change ($\Delta S°_{mic}$) mastered the micellization process, and the major parameter controlling the micellization is the transfer of the hydrophobic alkyl chain from the interior to the bulk of the micelle. That transfer declines the ($\Delta S°_{mic}$) to lower values because of the highly well-ordered chains in the micelles bulk.

Also, ΔS°_{mic} are small values which may be attributed to the neat structure of the prepared quaternary ammonium salts molecules which contributed in the micellar phase in PTEAAC.10 and PTEAAC.12 rather than PTEAAN.10 and PTEAAN.12. The highly ordered polymeric surfactants molecules proofed their firmness at which the hydrophobic alky chains are twisted in the micellar interior phase in a great compatibility, and the hydrophilic N^+ head group oriented to the water phase. Such an arrangement declines the repulsion in the surfactant-aqueous phase system which led to the noticed balance for the formed micelles[14, 25].

For Polymeric nonionic surfactants, The entropy of micellization ($\Delta S°_{mic}$) in these systems is slightly high positive indicates overall randomness in the systems due to a release of water molecules associated with hydrocarbon chains[26].

The micellization is endothermic ($\Delta H°_{mic} > 0$) and come to be exothermic ($\Delta H°_{mic} < 0$) at higher temperatures. Our results show that the negative value of $\Delta S°_{\mathrm{mic}}$is predominantly assigned to the large positive value of $\Delta S°_{\mathrm{mic}}$, particularly at low temperatures. Thus, the micellization is driven by $\Delta S°_{\mathrm{mic}}$. The increase in entropy of micellization in an aqueous medium can be related to the degree of rotational freedom of the hydrophobic alkyl chain of polymeric surfactant molecules in the non-polar interior of the micelle is much larger than that in the aqueous medium. In more details, the polymeric surfactant molecules migrated from the aqueous phase to the micelle when the configurational entropy of hydrophobic alkyl chain of the polymeric surfactant molecules went up [27].

3.3. Emulsification Power:

As shown in Table 4, for the polymeric cationic surfactants, the necessary time for separation of 90 % pure water at 25 °C will go up as the stability of the formed emulsion also increases. The emulsification power relies on the length of the hydrophobic chain. The PTEAAC.10 revealed reasonable emulsion stability (330s) while PTEAAC.12 with a long hydrocarbon chain displayed a lower value of emulsification power (100s). From the obtained result of emulsification measurements the synthesized polycationic surfactants noncable to form an emulsion, hence the synthesized polycationic surfactants predict their applicability in oil field without form stable emulsion with water that causes problems.

Table 4: Foam high, foam stability and emulsification power of the synthesized Polymeric surfactants at 25 °C.

Surfactant	Foam high, ML	Foam stability, (Sec.)	Emulsification power (Sec)
PTEAAN.10	4	100	Stable
PTEAAN.12	5	180	Stable
PTEAAC.10	8	290	330
PTEAAC.12	18	400	100

For polymeric nonionic surfactants, the surfactants containing longer nonionic chains formed stable emulsions with paraffin oil, while shorter chains exhibit a lower emulsion stability performance.

According to Table 4, The synthesized surfactants PTEAAC.12 exhibit low emulsification power nearly equal to 1.5 min. It can be used as a demulsifier, corrosion inhibitor and biocide in the oilfield system in which any chemical used should have a demulsifier ability to facilities the oil production processes., while the synthesized polymeric surfactants (PTEAAC.10, PTEAAN.10, and PTEAAN.12) has moderate or high emulsion stability. These polymeric surfactants can be used as emulsifier including textile industry, emulsion paints, and shampoos.

3.4. Foaming Power:

Foaming power of the prepared polymeric (cationic and nonionic) surfactants was recorded after stirring of 100 mL (0.1% conc.) of the polymeric surfactant solution energetically in a stoppered 200 mL cylinder at 25 °C according to Ross-miles method [28]. The data listed in Table 4, the synthesized polycationic surfactants have a tendency toward foam formation, and thus may be used in several applications such as additives in oilfield applications as antimicrobials and washing machine laundry.

The CMC of a surfactant is another indication for its efficiency as well as its foaming power; the lesser the CMC, the more efficient the surfactant as a foamer will be. Consequently, low CMC values lead to a more significant amount of foam than a surfactant, of the same series, with a higher CMC value. Another effect of CMC values is the foam stability, where the foam stability increases when the CMC values of the surfactant are low [16].

All the surfactants show better foam stability than the other solutions, But polymeric cationic surfactants better than Nonionic surfactant. Foamability for the prepared polymeric surfactants comes in the arrangement (PTEEAC.12 > PTEAAN.12) [28]. Foamability of nonionic surfactants depends on the CMC value (PTEAAN.12 > PTEAAN.10) and (PTEAAC.12 > PTEAAC.10) [16].

4. Conclusion

1- Two different types of polymeric surfactants (nonionic and cationic) were successfully prepared based on homopolymerization of triethanolamine acrylate monomer and characterized by FTIR, ^{1}H-NMR, ^{13}C-NMR spectroscopic techniques.

2- The surface-active parameters (CMC, $\boldsymbol{\pi_{\mathrm{cmc}}}$, $\boldsymbol{\Gamma_{\mathrm{max}}}$ and $\mathbf{A_{min}}$) and thermodynamic parameters ($\Delta\mathbf{G}^{\circ}_{\mathbf{mic}}$ and $\Delta\mathbf{G}^{\circ}_{\mathbf{ads}}$) of the aqueous solution by these surfactants were calculated at different temperatures.

3- The CMC of the polymeric cationic surfactants higher than the polymeric nonionic surfactants due to the presence of quaternary nitrogen, which increase adsorption of surfactant molecules at the interface. Moreover, increasing the alkyl chain length as well as temperature can decrease the CMC values.

4- Foaming and emulsification power show the superiority of polymeric cationic surfactants over polymeric nonionic surfactants.

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