Novel Cationic Polyurethane Surfactants Containing Saturated Chains- Part 1: Synthesis, Characterization and Surface Activity

Abstract

Novel cationic polymeric surfactants were synthesized throughout the reaction of monoester of triethanol amine and two saturated fatty acids (palmitic acid and stearic acid) and TDI (toluene diisocyanate). The obtained polyurethane (PU) then was reacted by acetyl chloride to yield the desired surfactants. The structures of the produced compounds were described by using Fourier Transform Infrared Spectroscopy (FTIR) and their average molecular weights. Silver nanocomposite of the prepared cationic PU surfactants were characterized via physical combination by chemically prepared silver nanoparticles. The structure of the silver composite was determined using: Ultra-violet spectroscopy, Transmission Electron Microscopy (TEM), and Dynamic Light Scattering (DLS) spectroscopy. The effect of the hydrophobic chains on the surface activities of the synthesized cationic polymeric surface active agents and their silver nanocomposite was studied.

Keywords

Polymeric surfactant; cationic; PU (polyurethane); nanocomposite; surface properties

Framework

PU polymers are playing an imperative character in many activities because of their generally going mechanical properties and their skill to be moderately easily machined and molded as plastics, foams and elastomers. In actual, urethane materials, such as foams and elastomers, have been establish to be well suited for many applications. The manufacture of PU includes the reaction between isocyanate groups (diisocyanate) and hydroxyl groups (polyol) leading to urethane groups. The second reaction is the gas manufacture by the reaction of isocyanate groups with water to form amine and carbon dioxide gas (chemical puffing cause) in the form of foams [1]. The PUs are three types: flexible foams when the used polyols molecular weights greater than 2500 g/mole; semi-rigid foams used polyols with molecular weights of 2000-6000 g/mole; while rigid foams used littler chain polyols with molecular weights of 200 to 4000 g/mole [2]. PU dispersions are polymer dispersions exhibit numerous benefits including the low instability of organic solvent, non-toxic and non-flammability properties [3]. For this object, PU dispersions gained detailed study and established to more environmental, recyclable and well-designed substrates [4]. Among all types of polyurethane dispersions, cationic polyurethanes are characterized by high resistivity near the hydrolytic effects of acid and alkali and can be used in the mixture of leather surfactant, dye dispersants and cloth dying agents [5]. Organic fatty acids are renewable, environmentally friendly and recyclable natural materials. The introduction of fatty acids, either clean acids or mixture of conformist fatty acids [6] into cationic PU polymeric chains growths their eco-friendly goods. Additionally, the attained compounds are provided more potential purposes such as revolving the polymer chains to extra homogeneous by organic compounds. These types make cationic polyurethanes more industrially arresting fresh material in the polyurethane industry. Cationic polyurethane was synthesized directly by the reaction of polyurethane ingredients with Tung oil [7]. Additional types of cationic PU were set by functionalized compounds enclosing hydroxylated Tung oil from ester and/or by reaction at the double bond [8]. Hydroxylated Tung oil is generally used in production of PU foam. Moreover, the existence of hydroxyl groups is solid to switch [3]. Cationic PU surfactants had best dispersity, film-forming facility and permanence [9], environmental affability [10]. In this study, cationic polyurethane surfactants and their silver nanocomposite were synthesized and their chemical structures were described using various analytical methods. The effect of the hydrophobic chains was examined on their surface activities.

2. Experimental Techniques

2.1 Materials

Triethanol amine (TEA), palmitic acid and stearic acid, toluene diisocyanate, acetyl chloride, $AgNO_3$ and trisodium citrate were purchased from Sigma Aldrich, Germany.

2.2 Surfactants synthesis

2.2.1 Synthesis of triethanol amine esters

Triethanol amine (0.10 mole, 14.91 g) and 0.10 mole of fatty acids (palmitic acid, 25.64 g, stearic acid, 28.44 g) were reacted in xylene (100 mL) using Dean-Stark connection and condenser. The reaction was progressed under heating condition (140 ^{o}C) to result 1.8 mL of water. Finally, the solvent was evaporated under reduced pressure at 70 ^{o}C [12]. The obtained esters were designated as TP and TS for pamlitate and stearate, respectively. The chemical structures of products were determined using FTIR spectroscopy (***Scheme 1***).

2.2.2 Synthesis of polyurethane derivatives

Triethanol amine esters (TP and TS) (0.20 mol) and toluene diisocyanate (0.10 mol) were dispersed in 2-butanone (80 mL) and were heated in 500 mL one necked flask at 140 ^{o}C for 24 h, then the reaction medium was permitted to cooled to room temperature. The solvent was stripped off under reduced pressure at 40 ^{o}C [11]. The yielded polyurethanes were washed twice by ethanol and dried in oven at 40 ^oC for 24 h, then designated as TPU and TPS for palmitate and stearate, respectively. The molecular weights of the synthesized polyurethanes were determined using HP-5890 gas chromatography provided with flame ionization detector, and the average molecular weights of the polyurethanes were found as 2650 and 2830 g/mole for TPU and TPS (***Scheme 2***).

2.2.3 Synthesis of cationic polyurethane surfactants

The cationic polyurethane surfactants were synthesized throughout the reaction of the different polyurethanes TPU and TPS and acetyl chloride as quaternizing agent in acetone as a solvent [12] to obtain the corresponding cationic surfactants which were designated as PUQP and PUQS for palmitate and stearate derivatives, respectively (***Scheme 3***).

2.2.4 Preparation of the Silver nanocomposites

The colloidal silver nanocomposites of the prepared cationic quaternary polyurethanes were assembled by silver nanoparticles obtained from chemical reduction of silver nitrate ($AgNO_3$) in using trisodium citrate as reducing agent [13].

2.3 Instrumentation

FTIR spectra were noted using Genesis Fourier modifier spectrophotometer FTIR^{TM}. Ultra violet-Visible spectra were noted at 200–800 nm using a 3–5 mm quartz pocket in Specord S-600 spectrophotometer (Analytik Jena AG). TEM spectroscopy was determined using JEM-(Jeol)-2000, Japan. Dynamic light scattering (DLS) was determined using Malvern zeta sizer nanoseries (Nano-ZS).

2.4 Measurements

2.4.1 Measurements of surface tension of the prepared surfactants

The determination of the surface tension values of the synthesized compounds was performed using de-attachment method by De-Nöuy Tensiometer Krüss K-6 equipped by a platinum ring. Different concentrations of the prepared cationic polyurethane surfactants in deionized water were measured in range of 10 to 0.01 mM at 25 ^oC. Average of three readings of the noticeable surface tension values were taken as the considered values, within 2 minutes interval between each reading [16].

3. Results and Discussion

3.1 Structure determination of the prepared intermediates and cationic surfactants

The chemical structures of the prepared intermediates and the cationic polyurethane surfactants were determined using FTIR spectroscopic analysis.

Figure 1A, B represents the FTIR spectra of the prepared triethanol amine palmitate and stearate. The spectra showed a characteristic broad absorption band at 3200-3500 cm^{-1}

characterized of O-H (carboxylic); appearance of a new band at 1724-1728 cm^{-1} for carbonyl group of the formed ester; 1124 cm^{-1} corresponds to C–O of the ester group.

Figure* 2a,BA,B** showed the FTIR spectra of the synthesized polyurethane (PUP) had the characteristic sharp absorption band at 3355cm^{-1} matched to stretching of N-H group; 2850 and 2923 cm^{-1} pointed out for symmetric and asymmetric stretching of C-H groups; the band at 1460 cm^{-1} corresponds to C=C aromatic ring of toluene diisocyanate moiety; 1353 cm^{-1} band attributed to stretching of C-N group and an absorption band appeared at 1106 cm^{-1} pointed out to the stretching of C-O ether group, ***Figure 2A, B.

Figure 3A,B represents the FTIR spectra of the synthesized cationic polyurethanes. The spectra showed similar absorption bands for the triethanol amine polyurethanes and also the appearance of a new absorption band at 1331, 1322 cm^{-1} corresponds to $C\text{-}N^+$, which proves the formation of the quaternary cationic derivatives of palmitate derivative (***Figure 3A***) and stearate derivative (***Figure 3B***).

FTIR spectroscopic analysis of the prepared esters and polyurethanes and their cationic derivatives were proved their chemical structures as represented in ***Schemes 1-3***.

3.2 Structure determination of the prepared nanocomposites

3.2.1 Dynamic light scattering (DLS)

The cationic silver nanocomposites were illustrated using DLS. Generally, DLS studies of the synthesized nanocomposite existing bimodal deliveries, ***(Figure 4A-B)***. The scattering had a main peak at certain particle size diameter with area intensity % for each nanocomposite. PUQP = 142 nm (95% area intensity) and PUQS = 118 nm (66% area intensity), ***Table 1***. Size (counting size distribution) and zeta potential are essential characteristic parameters for nanocomposites formation [17].

In agreement with the obtained particle size diameter distribution (by number) ***(Figure 5A,-B)***, the particle size was 155 nm for PUQP, and 63 nm for PUQS, silver nanocomposite. Noticeably, the particle size diameter range of the synthesized nanocomposite based on the chains of fatty acid incorporated in the polyurethane cationic derivatives [17]. The Fatty acid chains are dependable for the shield of the formed nanocomposite. Expanding the Fatty acid chain length raises the inter-particle distance between the formed silver nanocomposites. That avoids their congealing and consequently reduces the diameter of the assembled nanocomposites, ***Table 1***. The obtained particle size diameters of the nanocomposite can be organized in the order: PUQSN < PUQPN.

The polydispersity index (PDI) describes the particle size distributions of the nanocomposite. Larger values of PDI than 1 PDI values higher than 1 pointed out to the scattering of the assembled nanocomposites diameter with little intensity; though the smaller PDI values than unity are specified to narrow nanocomposite diameters. It is well-defined that PDI of the synthesized nanocomposites is lower than 1, showing the narrow size, uniform diameters and low scattering of the assembled nanocomposites. Clearly, PDI values are always raised for long fatty acid chain and ranged between 0.44 and 0.46 ***(Table 1)***. Rising PDI values by increasing the Fatty acid chain length shows the narrow size distribution of the molded nanocomposite.

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Zeta potential (ZP) terms the complete surface charge of the nanocomposite in their colloidal system. The aqueous phase around the nanocomposite is separated into two regions; the inner region of the Stern layer where the counter ions are powerfully confined, and the outer region where the counter ions are less connected. Inside the outer layer, there is a boundary at which the ions and particles are stable [18]. Once nanocomposite change by the effect of gravity, ions within the inner boundary change. Potential between the boundaries of the Stern layer and the diffused layer is the described as zeta potential. Zeta potentials give an idea about the potential strength of the formed nanocomposite colloidal systems. High negative or positive zeta potentials of the particles in the colloidal solutions repel these particles and there will be no inclination for the particles [19]. Obstinately, low zeta potential ranges of the particles will increase the particles coagulation [20]. ZPs of the prepared cationic polyurethane nanocomposite ***(Table 1)*** are in negative values and in the range of -24.4 to -27.20 mV, indicating the stability of the assembled nanocomposite in their colloidal solutions. By other words, the coagulation of the nanoparticles is hardly happen. The results are in accordance with PDI and the particle size distribution values.

3.2.2 Transmission Electron Microscope (TEM)

The dimensions and morphology of the synthesized silver nanocomposite polyurethane cationic surfactants (PUQS and PUQP) were detected using transmission electron microscope (TEM). TEM image of the prepared silver nanoparticles indicated their spherical forms with narrow diameters, which indicates the uniform, spherical and mono-dispersed silver nanoparticles. ***Figure 6*** displays the TEM images of the prepared cationic polyurethane nanocomposites. ***In Figure 7A-,B*** it can be seen from TEM spectroscopy that the particles are non-uniform in shape and have a particle size distribution in various ranges provisional on the saturated chain length of each cationic surfactant. It is obvious also that the diameter and shape of the silver nanoparticles did not variation after creation of the changed nanohybrids.

Capping of silver nanoparticles by the changed cationic polyurethane Palmitate and stearate provides high protection of the silver nanoparticles. That can be monitored as no aggregation was happened for the silver nanoparticles. The diameter of the silver-cationic polyurethane Palmitate and stearate nanohybrids was increased gradually by increasing the fatty acid chain length. The fixing of the silver nanoparticles diameters was provided by contact with the cationic chains. While the aggregation prevention was delivered by the electrostatic repulsion occurred between the capped nanocomposites. That is in a good agreement with the values of zeta potential found from dynamic light scattering values ***(Table 1)***.

3.2.3 Ultraviolet-Visible spectroscopy (UV-Vis)

The assembling of silver nanocomposite of the prepared polyurethane cationic surfactants was detected using UV-Vis spectra. It is obvious in ***Figure 8*** the presence of a strong absorption peak at 430 nm which is corresponded to the synthesized silver nanoparticles. The presence of the UV-Vis absorption peak of the pure silver nanoparticles is due to the plasma shell formed around the nanoparticles, which is occurred due to the absorption of the counter ions present in the medium of reduction reaction of $AgNO_3$ [19]. The absorption peak of silver nanoparticle is quite symmetric in 360-570 nm, which implies that the diameter of the silver nanoparticles size formed during the reduction reaction is narrow. ***Figure 8*** displays also the UV spectra of silver nanocomposite assembled by PUQP and PUQS cationic surfactants as stabilizing agent. The spectra of silver nanocomposite of the polyurethane cationic surfactants have individual absorption bands maxima in the range of 410-430 nm, which attributed to the plasmon adsorption of silver nanocomposite of polyurethane cationic surfactant. The surface plasmon absorption band is owing to the aggregation of silver nanocomposite in the surfactants solutions. The surface plasmon absorption band of silver nanoparticles vanished by the addition of the different cationic surfactants at 415 nm. Silver nanocomposites in their colloidal dispersions are positively charged due to the effect of the adsorbed counter ions on their surface. The assembling of the different cationic surfactant molecules on the silver nanocomposite prevents the aggregation of the silver nanoparticles during their Brownian motion and collision in their colloidal solutions [13].

3.3 Surface activity

3.3.1 Surface activity of polyurethane cationic surfactants.

Figure 8**:-** represents the surface tension versus –log concentration of the assembled cationic polyurethane palmitate and stearate surfactants in deionized water at 25 ^{o}C. It is shown that the behavior of the cationic surfactants is normally as the conservative cationic surfactants with the two characteristic regions, pre- and post micellar regions. The critical micelle

concentration (CMC) ideals of these surfactants were **mined** obtained using extrapolation technique and they are registered in ***Table 2***. The **got** CMC values **were** ranged between 1.106 mM for PUQP and 0.07 mM for PUQS. CMC values are decreased gradually by increasing the fatty acid chain length from palmitic to stearic acid. The magnitude of CMC values registered in ***Table 2*** revealed that the assembled cationic surfactants are micellized at concentrations like to some conventional cationic surfactants. [21], BRIJ 35 (0.09 mM) [22] and Triton X-100 (0.2 mM) [23]. The maximum CMC value was **got** displayed for PUQP at 1.106 mM, while growing the fatty acid chain length decreases their CMC values considerably to obtain CMC of PUQS at 0.07 mM at 25 °C. The reduction in CMC ranges can be attributed to the rise of the molecules hydrophobicity by increasing the repeated methylene groups in the fatty acid chains from 15 methylene group in PUQP to 18 groups in PUQS. The **supreme** utmost surface excess (Γ_{max}) fixes the maximum concentration of surfactant molecules at the saturate air/water interface **at saturation**. The highest surface excess value fixes the ability of surfactant molecules to adsorb at the solution interface, and consequently the sequence of surface tension reduction in the surfactant solution will be parallel to the rise of surface excess values. The maximum surface excess of the assembled cationic polyurethane surfactants registered in ***Table 2*** were deliberate based on their surface pressure ranges (Γ_{max}) using equation (1).

$$\boldsymbol{\Gamma_{max} = -\,(1/nRT)\,(d\gamma/d\ln C)} \qquad (1)$$

AnywhereWhere**:** $d\gamma/d\ln C$ is supreme slope and R, T, C are gas constant, temperature and concentration swelling the polyurethane chain length from 2 to 6 units raises the surface concentration to the maximum at 6 polyurethane units. A good relation is presented between the surface tension **ranges** and the **supreme** surface excess concentration. Increasing of fatty acid chains reductions the surface tension of surfactant solution due to the rise of the maximum surface concentration at the interface. The tendency towards adsorption at the interface is governed by the degree of hydrophilcity and lipophilicity of the surfactant molecules, which is uttered in term of HLB ranges. Hydrophilic-lipophilic balance (HLB) limits the behavior of the many cationic surfactants in their solutions [24] [37]. Oil soluble surfactants had HLB values in the values of 1-7, water dispersible surfactants had HLB in the range of 7-14, and water soluble surfactants had HLB in the range of 14-20. Surfactants with higher HLB values than 16 are effectual as solubilizing agents [25] [38]. Scheming the HLB values of the prepared cationic surfactants ***(Table 2)*** using Griffin's method [26] shows their high tendency to disband in aqueous medium and also their high solubilizing leaning.

3.3.2 Surface activity of polyurethane cationic surfactants nanocomposites.

Surface activity is **R**representsed by the surface tension versus -log concentration of the cationic polyurethane palmitate and stearate nanocomposite at 25 ^{o}C. It is **strong** evident that the colloidal **solutions** nanocomposite solutions of the cationic surfactants ha**s**ve lower surface activity than the fathers of the nanocomposite (PUQPN and PUQSN). The lowering in the surface activity can be resolute from the relatively higher surface tension ranges. The rise in the surface tension values of the nanocomposite than the parent cationic surfactants can be ascribed for three reasons. Firstly, **decrease** the diameter decreasing of the shaped nanocomposite ***(Table 3)*** rises the fraction between each other which reductions their motion in the colloidal solutions and also their pumping into the air-water interface [27],[35]. As a data, a strong cohesive force everyday between the molecules, which follow-on higher surface tension for the nanohybrids colloidal solutions.

Secondly, when the concentration of the nanocomposite in the cationic polyurethane colloidal solutions increases, the spacing between the nanocomposites is **compact** filled [28], [36]. Hence, an attractive **V**van der Waals force is employed over the electrostatic repulsion force between the molecules which increases the surface tension of the cationic polyurethane nanocomposite in the colloidal solutions. Finally, the smaller nanocomposite exhibition, the higher the surface charge density liken to the larger nanocomposite [29]. As a result, the electrostatic repulsion forces between the nanocomposite and the aqueous phase rise. That enhances the adsorption into the air-water surface, which decreases the surface tension of smaller size nanocomposite [30]. Moreover, when the particle size of the cationic polyurethane nanocomposite increases, the surface area and the surface free energy reductions, this raises the surface tension of the nanocomposite colloidal solutions.

Conclusion

The manuscript showed some concluding points:

1- Polyurethane cationic surfactants were prepared by the reaction of triethanol amine monoester and toluene diisocyanate followed by quaternization with acetyl chloride.

2- The chemical structures of the prepared compounds were determined using FTIR spectroscopy.

3- Silver nanocomposites of the prepared compounds were prepared by the assembling the cationic surfactants on silver nanoparticles.

4- The silver nanocomposites were characterized using UV and dynamic light scattering and TEM analysis.

5- The surface activity of the prepared cationic surfactants was determined by measuring their surface tension values.

REFERENCES

[1] Nabel A. Negm, Maher A. El Hashash, Mona A.Youssif, Eid A. Ismail, Zizi I. Abdeen, Nasser R. Abdel Rahman. "Novel nonionic polyurethane surfactants and Ag- nanohybrids: Influence of nonionic polymeric chains" J Surfact Deterg, 11743-016-1909-5(2016).

[2] Chang LC, Xue Y, Hsieh FH "Comparative study of physical properties of water blown rigid polyurethane foams extended with commercial soy flours. J Appl Polym Sci 80:10-19 (2001).

[3] Ako M, Kennedy J P "Poly isobutylene-based urethane foams. I. Synthesis and properties of novel poly isobutylene-based flexible polyurethane foams”. J Appl Polym Sci, 37:1351-1361(1989).

[4] Lligadas G, Ronda JC, Galià M, Cádiz V " Novel Silicon-Containing Polyurethanes from Vegetable Oils as Renewable Resources: Synthesis and Properties”. Biomacromol 7:2420-2426(2006).

[5] Guo YS, Ma XY, Wu Z, Zhang SF, Yang XP " Synthesis and Modified of Nonionic Waterborne Polyurethane for Synthetic Leather." China Leather 42:47-57(2013).

[6] Naghash HJ, Iravani M, Akhtarian R” Synthesis and characterization of monoallyl-end-capped diethylene oxide-based polyurethane surfactant". Synthesis and Reactivity in Inorganic Metal-Organic and Nano-Metal Chemistry 44:927-934(2014).

[7] Meiorin C, Mosiewicki MA, Aranguren MI "Ageing of thermosets based on tung oil/styrene/divinylbenzene". Polymer Testing 32:249-255 (2013).

[8] Silva V R, Mosiewicki MA, and Yoshida MI "Polyurethane foams based on modified tung oil and reinforced with rice husk ash I: Synthesis and physical chemical characterization. Polymer Testing " 32:438-445(2013).

[9] Zaky M. F., Badawi A. M., Sabbah I. A., Abdelghani R. A. and Hendawy M. E., Synthesis, Characterization and Surface Activities of Cationic Polysaccharide (Aloe) Schiff Base Surfactants. J Surfact Deterg 18, 455-461 (2015)

[10] Rosen M. J., Surfactants and interfacial phenomena, 2nd edn. Wiley, New York (1989).

[11] Hany, M. A., Ahmed H. T. and Antar A. A, "Novel Quaternary Ammonium-Based Cationic Surfactants: Synthesis, Surface Activity and Evaluation as Corrosion Inhibitors

for C1018 Carbon Steel in Acidic Chloride Solution. J Surfact Deterg, 20, 735–753 (2017).

[12 Nabel A. Negm, Aiad, I. A. and Tawfik, S. M., Screening for potential antimicrobial activities of some cationic uracil biocides against wide spreading bacterial strains. J Surfact Deterg 13:503–511 (2010).

[13] Shokry SA, El Morsi AK, Sabaa MS, Mohamed RR, El Sorogy HE "Synthesis and characterization of polyurethane based on hydroxyl terminated polybutadiene and reinforced by carbon nanotubes". Egypt J Petrol 24:145-154(2015).

[14] Nabel A. Negm, Mahmoud SM "Synthesis, surface and thermodynamic properties of carboxymethyl (di-2-ethanol) ethyl alkanoate ammonium bromide amphoteric surfactants". Egypt J Petrol 14:79-88(2005).

[15] Azzam EMS, El-Frarrgy AF, Ismail DA, Abd Elaal AA "Detection of heavy metal ions using synthesized amino thiol surfactants assembled on gold nanoparticles". J Dispers Sci Technol 32:816-822(2011).

[16]. Wang C, Huang X, Deng W, Chang C, Hang R, Tang B "A nano-silver composite based on the ion-exchange response for the intelligent antibacterial applications". Mater Sci Eng C Mater Biol Appl 41:134–141(2014).

[17] Paredes D, Ortiz C, Torres R "Synthesis, characterization, and evaluation of antibacterial effect of Ag nanoparticles against Escherichia coli O157:H7 and methicillin-resistant Staphylococcus aureus (MRSA)". Int J Nanomedicine 9:1717–1729(2014).

[18] Nabel A. Negm, El-Frarrgy AF, Mohammad IA, Zaki MF, Khowdiary MM "Synthesis and inhibitory activity of Schiff base surfactants derived from tannic acid and their cobalt (II), manganese (II) and iron (III) complexes against bacteria and fungi". J Surfact Deterg 16:767–777(2013).

[19] Müller RH, Jacobs C, Kayser O “Nanosuspensions as particulate drug formulations in therapy. Rationale for development and what we can expect for the future”. Advanced Drug Delivery Reviews -47:3 – 19(2001).

[20] Zhang Y, Yang M, Portney NG, Cui D, Budak G, Ozbay E, Ozkan M, Ozkan CS. " Zeta potential: a surface electrical characteristic to probe the interaction of nanoparticles with normal and cancer human breast epithelial cells" Biomed Microdevices 10:321–328(2008).

[21] Ho J, Danquah M. K, Wang H, Forde GM” Protein loaded mesoporous silica spheres as a controlled delivery platform”. J Chem Technol Biotechnol 83:351–358(2008).

[22] Hedberg J, Lundin M, Lowe T, Blomberg E, Woold S, Wallinder IO J Colloid Interfac Sci 269:193-201(2012).

[23] Hait SK, Moulik SP "Determination of critical micelle concentration (CMC) of nonionic surfactants by donor-acceptor interaction with lodine and correlation of CMC with hydrophile-lipophile balance and other parameters of the surfactants". J Surfact Deterg 4:303-309(2001).

[24] Hafiz, A. A., Badawi A. M., El-Deeb F. I., Soliman, E. A. and El-Awady, M. Y., Ferrocene-based cationic surfactants: surface and antimicrobial properties. J Surfact Deterg 13, 165–172 (2010).

[25] Kuperkar, K., Modi, J. and Patel, K., Surface-active properties and antimicrobial study of conventional cationic and synthesized symmetrical Gemini surfactants. J Surfact Deterg 15, 107–115 (2012).

[26] Perez, L., Pinazo, A., Pons, R. and Infante, M., Gemini surfactants from natural amino acids. Adv Coll Interface Sci., 205,134–155. (2014).

[27] Aiad, I. A., Badawi, A. M., El-Sukkary, M. M., El-Sawy, A. A. and Adawy, A. I., Synthesis and biocidal activity of some naphthalene-based cationic surfactants. J Surfact Deterg 15, 223–234(2012).

[28] Yongbo, S., Qiuxiao L., Yunling, L. and Lifei, Z., Biological Behaviors of Guanidine-Based Cationic Surfactants. J Surfact Deterg 17, 459–464 (2014).

[29] Miao S, Callow N, Dashtbozorg SS, Salager JL, Ju LK Ethylation of Di-rhamnolipids: A Green Route to Produce Novel Sugar Fatty Acid Nonionic Surfactants. J Surfact Deterg 17:1069-1080(2014).

[30] Nabel A. Negm, Ahmed F. Elfarrargy, Ahmed M. Elsabag and Nasser R. Abdelrahman. "New Schiff Base Cationic Surfactants: Surface and Thermodynamic Properties and Applicability in Bacterial Growth and Metal Corrosion Prevention". J Surfact Deterg 14:505–514(2011).

[31] Tanvir S, Qiao L "Surface tension of Nanofluid-type fuels containing suspended nanomaterials". Nanoscale research letters 7:1-10(2012).

[32] Vafaei1 S, Purkayastha A, Jain A, Ramanath G, Borca-Tasciuc T" The effect of nanoparticles on the liquid–gas surface tension of Bi_2Te_3 nano fluids". Nanotech 20:185702(2006).

[33] Abbas Z" Size-dependent surface charging of nanoparticles". J Phys Chem C 112:5715-5723(2008).

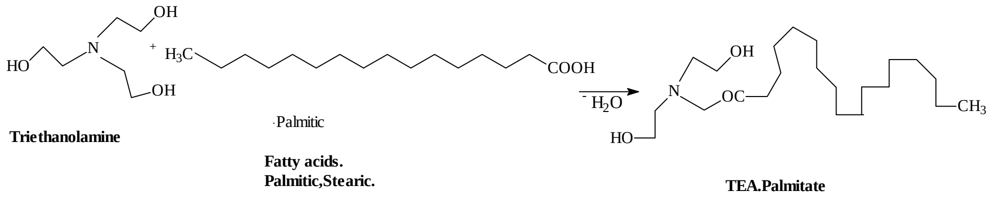
[34] Brown MA Effect of surface charge density on the affinity of oxide nanoparticles for the vapor–water interface. Langmuir 29:5023-5029(2013).

[35] Daria Wie. ,Adam Dob.,Katarzyna Sta.,Patrycja Dub.“Synthesis,Surface and Antimicrobial Activity of Piperidine-Based Sulfobetaines. J Surfact Deterg 20-1-151–158(2017).

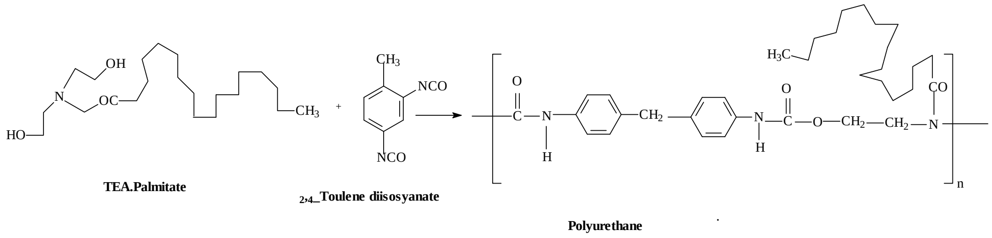
[36] Mohammed Abo-Riya, Ahmed H. Tantawy, Wagdy El-Dougdoug.” Synthesis and evaluation of novel cationic gemini surfactants based on Guava crude fat as petroleum collecting and dispersing agents”J of Molecular Liquids 221-642:650(2016).

[37] A. Abdelmajeid, Mahasen S.Amine,Reda A. Hassan” Fatty Acids in Heterocyclic Synthesis. Part XVII: Synthesis of Non Ionic Surfactants Containing Piperidine, Piperazine, and Imidazole Based on Thiadiazole and Microbiological Activities Evaluation. nternational Journal of Organic Chemistry 7: 346-368, (2017).

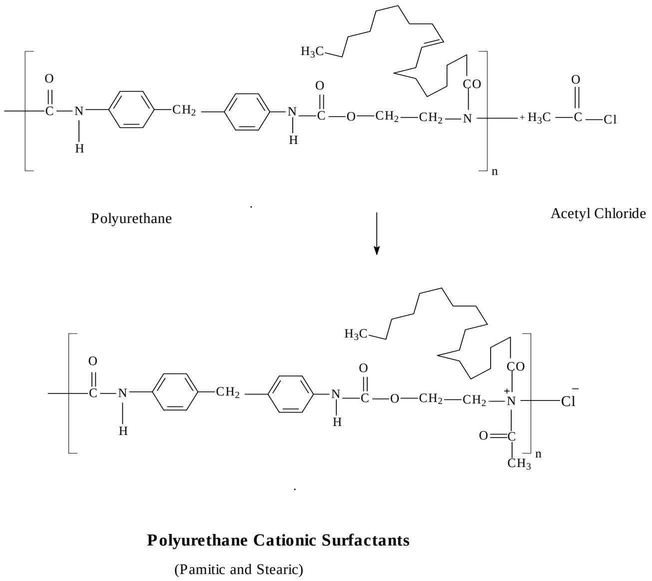
[38] Katarzyna E. Greber.” Synthesis and Surface Activity of Cationic Amino Acid Based Surfactants in Aqueous Solution” . J Surfact Deterg 20-1189:1196(2017).



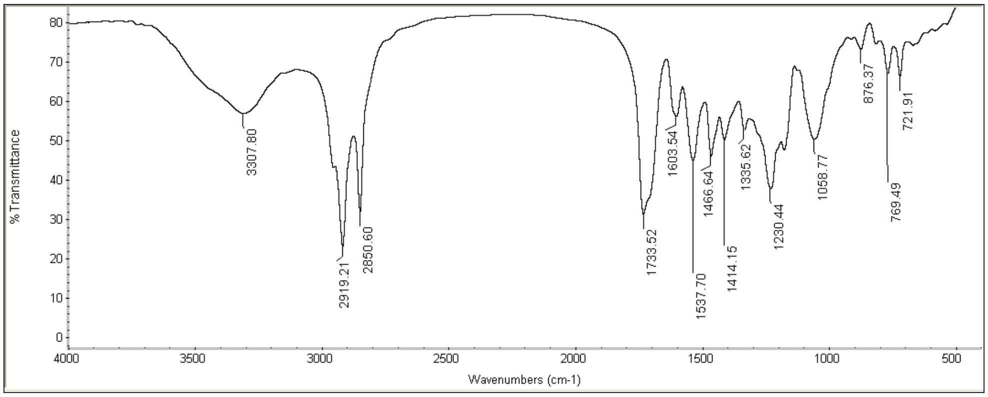
Scheme 1: Structure of monoester saturated chain palmitate and stearate.



Scheme 2: Structure of Polyurethane saturated chain palmitate and stearate



Scheme 3: Structure of Polyurethane cationic surfactants saturated chain palmitate and stearate.



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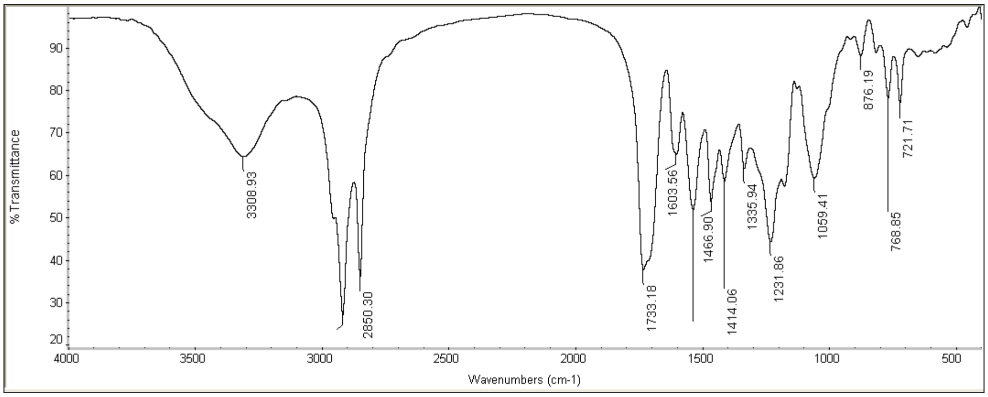
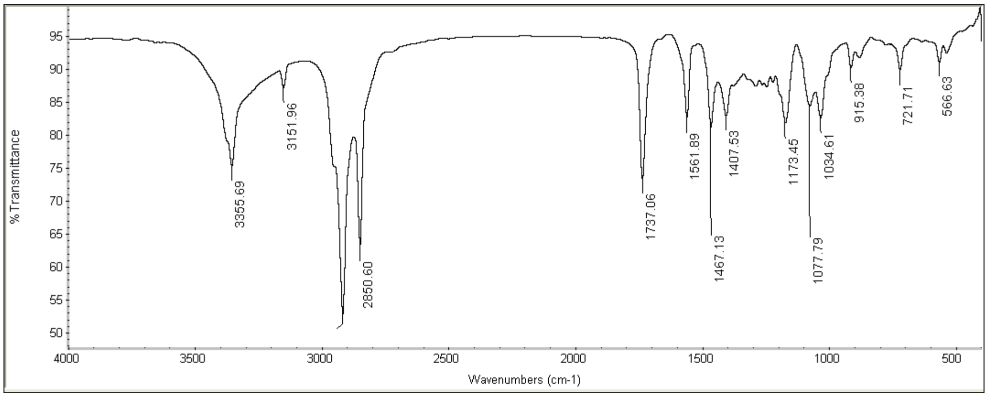
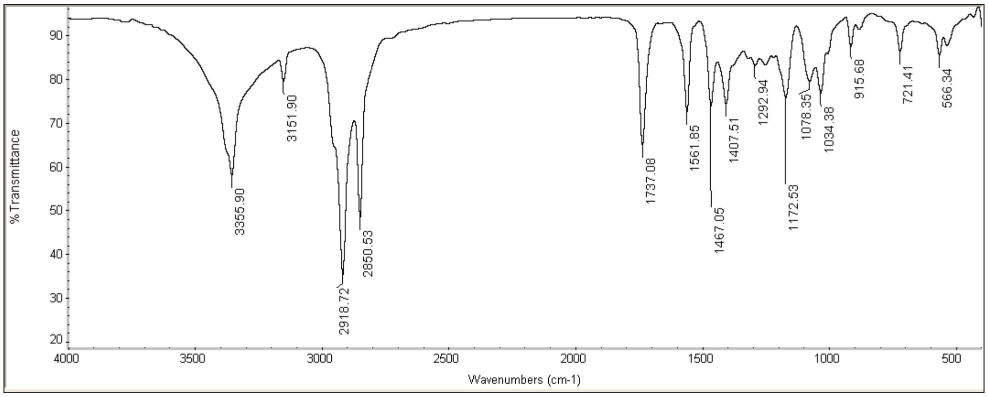


(B)

Figure 1: IR spectra of: (A): Ester triethanol amine Palmitic (TEAP), (B): Ester triethanol amine Stearic (TEAS).

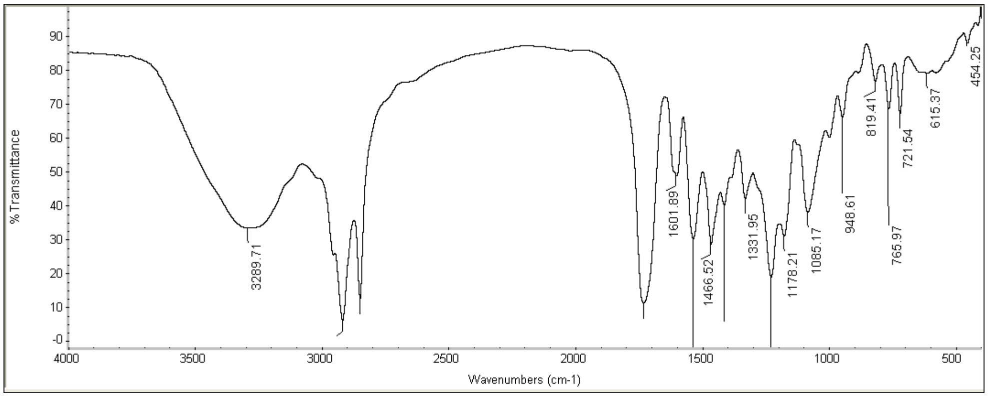


(A)

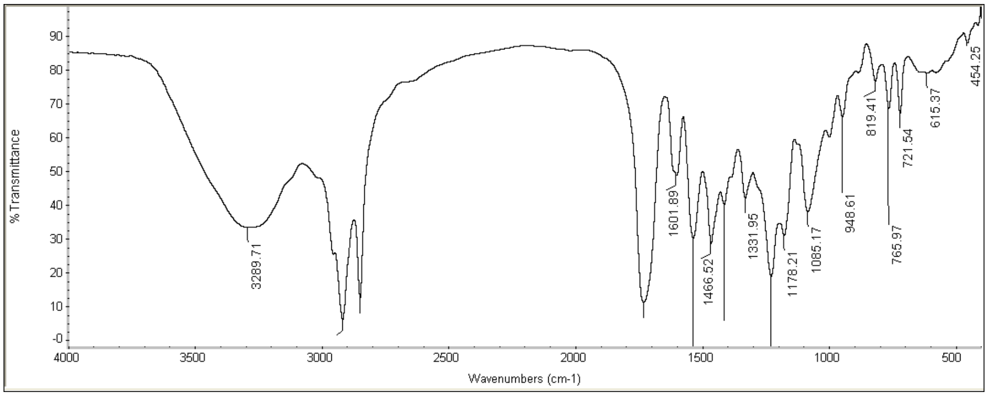


(B)

Figure 2: IR spectra of: (A): Polyurethane palmitate (PUP), (B): Polyurethane stearate (PUS).

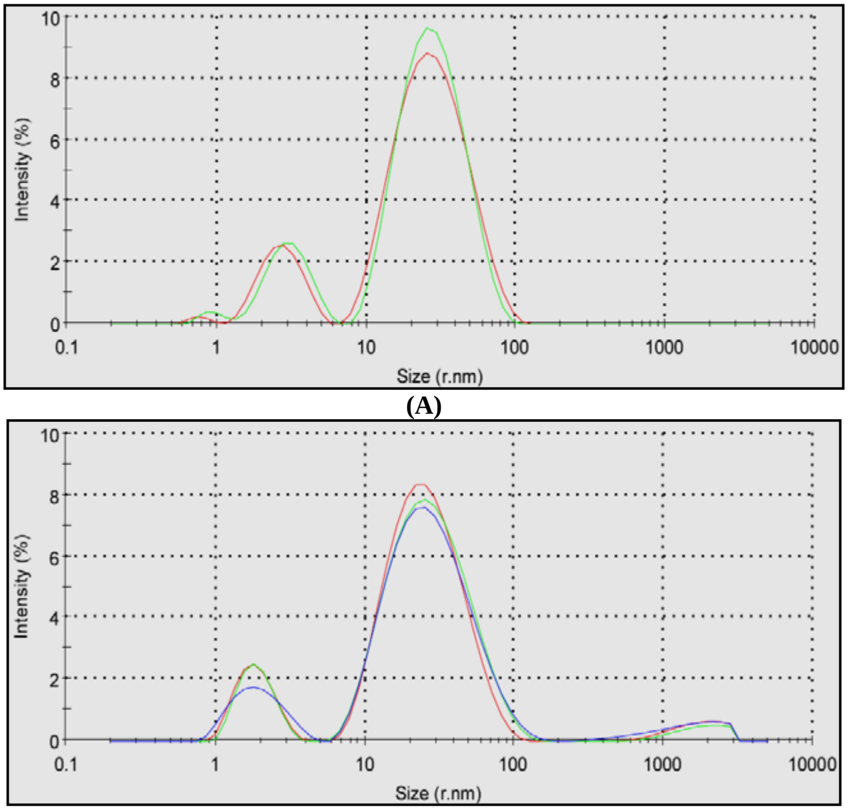


(A)



(B)

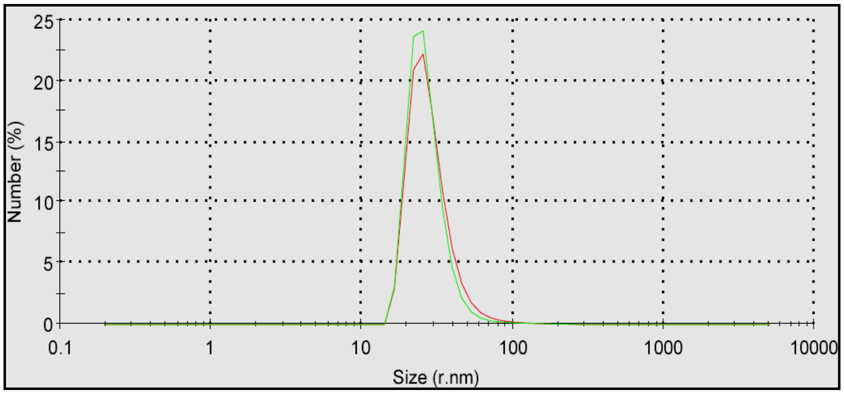
Figure 3: FTIR spectra of A: Cationic polyurethane palmitate (PUQP), B: Cationic polyurethane stearate (PUQS).



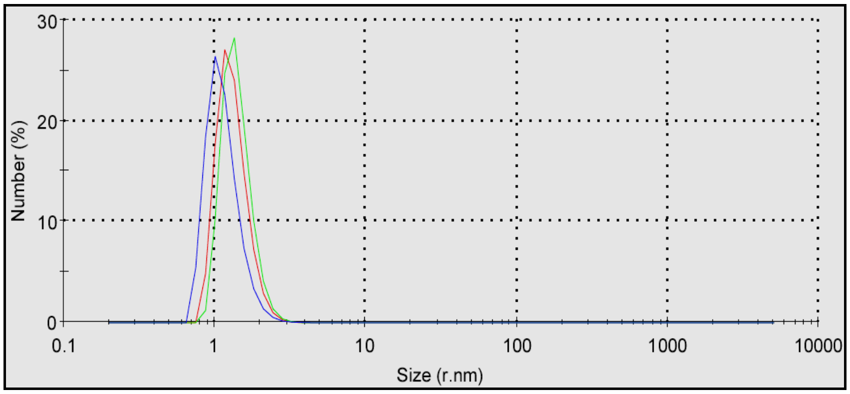
(A)

(B)

Figure 4: Particle size distribution profile by intensity for silver nanocomposite of: (A) PUQPN and (B) PUQSN.

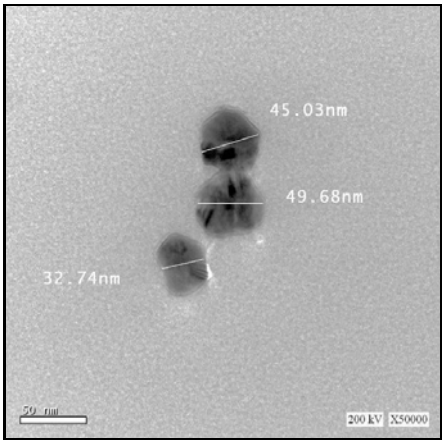


(A)



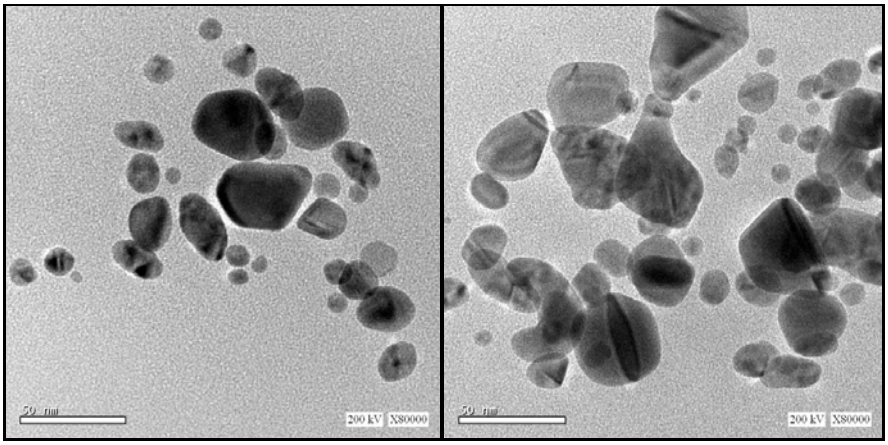
(B)

Figure 5: Particle size distribution profile by number for silver nanocomposite of: (A) PUQPN and (B) PUQSN.



SNP

Figure 6: TEM graphs of the prepared Silver nanoparticles.



PUQNS PUQNP

Figure 7: TEM graphs of the prepared cationic polymeric surfactants PUQSN and PUQPN.

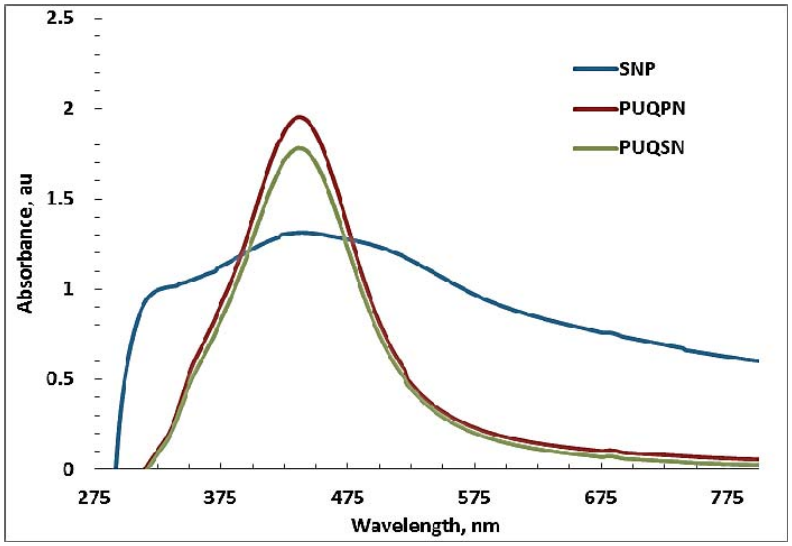


Figure 8: UV-Vis spectra of the synthesized silver nanoparticles (SNP) and polyurethane cationic surfactants nanocomposites for PUQSN and PUQPN.

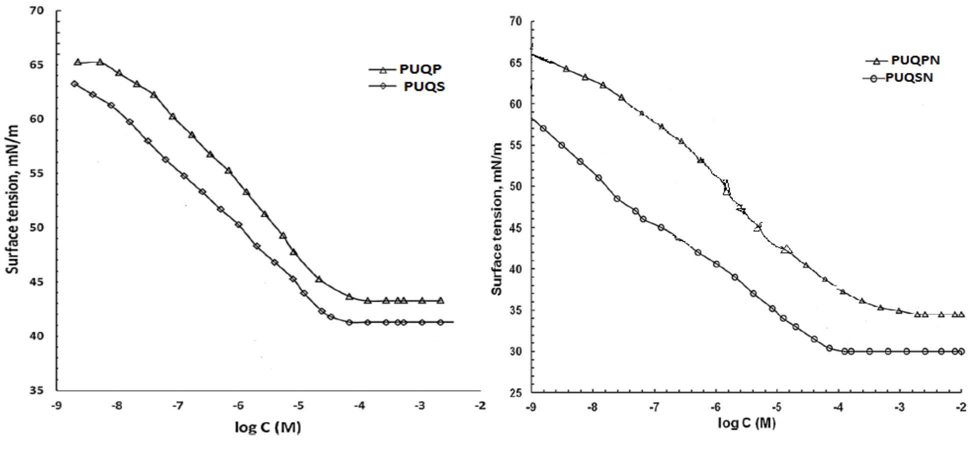


Figure 9: Variation of surface tension against Log concentration of the synthesized polyurethane cationic surfactants PUQ, PUQP and their nanocomposites PUQSN, PUQPN.

Table1: Particle size of the synthesized nanocomposite of cationic polyurethane surfactants.

Cationic surfactant	Particle size by intensity		Particle size by number	Polydispersity index, PDI	Zeta potential, mV
	Diameter, nm	%	Diameter, nm		
PUQPN	142	94	155	0.44	-24.4
PUQSN	118	66	63	0.46	-27.2

Table2: Surface parameters of the synthesized polyurethane cationic surfactants.

Cationic Surfactant	CMC, M	HLB	pC_{20}	Γ_{max},
PUQP	$1.106x10^{-3}$	17.8	$5.25x10^{-5}$	$9.183x^{-11}$
PUQS	$2.521x10^{-4}$	19.2	$3.55x10^{-6}$	$1.203x^{-10}$

Table3: Surface parameters of the synthesized polyurethane cationic surfactants nanocomposites.

Cationic Surfactant	CMC, M	pC_{20}	Γ_{max},
PUQPN	$2.14x10^{-4}$	$7.49x10^{-5}$	$9.859x^{-11}$
PUQSN	$1.38x10^{-4}$	$2.471x10^{-5}$	$9.726x^{-11}$