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New Cationic Gemini Surfactants and Their Use as Dispersants in Oil-in-Water (O/W) Emulsions

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Abstract:

In the current research, two types of new cationic gemini surfactants with different spacers (aromatic and heterocyclic) derived from epichlorohydrine were prepared.

The prepared compounds were characterized using FTIR and ^{1}H-NMR spectroscopy. Then the value of critical micelle concentration CMC was calculated using the electrical conductivity and preparing a series of molar concentration of the new surfactants, as well as calculating the balance value between the hydrophilic and hydrophobic (lipophilic) HLB groups.

Cationic gemini surfactants were tasted at different concentration 20-40 ppm by preparing dishes for oil-in-water emulsions determine their dispersion efficiency. It was observed that the dispersant containing the heterogeneous ring (**MS1**) was more efficiently dispersed than the surfactant containing the aromatic ring (**MS2**) in the presence of the same hydrocarbon chain and at a concentration of 40 ppm.

Keywords: Quaternary ammonium salts and Heterocyclic spacer.

1. Introduction:

Gemini surfactants, dimeric quaternary ammonium salts, represent a new class of cationic surfactants. These compounds consist of two monomeric moieties, a hydrophilic head group (positively charged nitrogen atom) and a hydrophobic part (long alkyl chain) [1,2], connected by a flexible or rigid spacer [3]. Gemini surfactants exhibit superior surface, interfacial and biological properties than their conventional monomeric analogues [4,5]. Critical micelle concentration (CMC) of gemini surfactants is much lower compared to the CMC values of monomeric surfactants [6]. Lower critical micelle concentration means that the same effect can be reached by using lower amount of the gemini surfactant [7]. Elongating the alkyl chain decreases the CMC for Gemini surfactants [8–10] while adding heteroatoms or multiple bonds into the spacer increases the CMC value [3,9,11]. On the other hand, an increase in the spacer length can either lead to an increase or decrease in the CMC depending on its length, flexibility and the nature of groups it incorporates [12–16]. Ammonium-based cationic gemini surfactants are successfully applying in multiple oilfield applications [17]. This structure owns more advantages, such as higher surface tension, higher micelle forming ability, and better water solubility [18].

In this study, cationic surfactants were prepared from the reaction of epichlorohydrine with 4-aminopyridine to produce dispersion **MS1** and with 1,4-dihydroxybenzene to produce dispersion **MS2** using a hydrocarbon chain consisting of 12 carbon atoms. After conducting CMC measurements and conducting laboratory test on oil-in-water emulsions, it was found that the **MS1**dispersion has a higher dispersion efficiency than **MS2**.

2. Experimental:

2.1- Materials and Instruments:

Materials: Epichlorohydrine (Aldrich, 99%), 14-dihydroxy benzene (Sigma-Aldrich, 98%), 4-aminopyrdine (GT-Paker, 98%), dimethyl amine (LAB-SCAN, 98%), 1-bromo dodecane (Fluka, 98%), sodium hydrogen sulfate (Merck, 99%), potassium hydroxide (Merck, 98%), chloroform (Hi Media, 99%), ethanol (Merck, 99%) and anhydrous magnesium (Merck, 99%) sulfate. All the chemicals were used without further purification.

Instruments: Bruker-400 ^{1}H-NMR spectrometer, Shimadzu-(4000-400) FTIR spectrometer, Jenway PCM3 conductivity, Magnetic heating stirrer and Rotary evaporator.

2.2- Synthesis of MS1: (N,N'-((pyridin-4-ylazanediyl)-bis-(2-hydroxypropane-3,1-diyl))-bis-(N,N-dimethyldodecan-1-aminium) bromide:

It was prepared in **three** steps. The **first** step: In 150mL round flask, gradually add (47mL, 0.6mol) epichlorohydrine into a mixture consisting of (28g, 0.3mol) 4-aminopyridine and 10ml ethanol. It is stirred for (10min) in an ice bath until the addition process is completed. The mixture is then raised under reflux distillation for 10hrs, then a rotary evaporator is used to remove the solvent in a water bath at a temperature 40°C for an hour until a yellow-colored liquid is obtained with a result of (63%) [19].

The **second** step: (3g, 0.01mol) of the compound resulting from the first step is taken and the mixture consisting of (1.5mL, 0.02mol) dimethyl amine and (0.67g, 0.012mol) of potassium hydroxide is gradually added in drops with continuous stirring at room temperature until it forms a precipitate. After that, the mixture is filtered and the filtrate is taken and placed in a separation funnel and extract it with chloroform, then dry the product using anhydrous magnesium sulphate, then evaporate the product to remove the solvent for the purpose of obtaining a yellow oily liquid with a yield of (58%) [19].

The **third** step: (3g, 0.01mol) of the compound prepared in the second step is add to the reaction flask containing (5mL, 0.02mol) 1-bromododecane and 50mL ethanol at room temperature. The mixture was placed under reflux distillation at 80-90°C for an hour, until a white viscous liquid is obtained with a result of (53%) as shown in Figure 1, [19].

2.3- Synthesis of MS2: N,N'-((1,4-phenylenebis(oxy))-bis-(2-hydroxypropane-3,1-diyl))-bis-(N,N-dimethyldodecan-1-aminium) bromide

It was prepared in **three** steps. The **first** step: Add (47mL, 0.6mol) epichlorohydrine drop wise at 0°C to the mixture consisting of (25.5g, 0.3mol) 1,4-dihydroxy benzene, (1g, 0.8mol) of sodium hydrogen sulphate, and (0.6mL) water in a 150mL round flask. Then the mixture is heated under reflux distillation with continuous stirring for 5hrs, until obtaining a yellow-colored liquid is obtained with the result (61%) [19]. As for the second and third steps, they are the same method for preparing MS1, where products obtained with (59%) and (55%) respectively, with a chemical composition shown in Scheme 1.

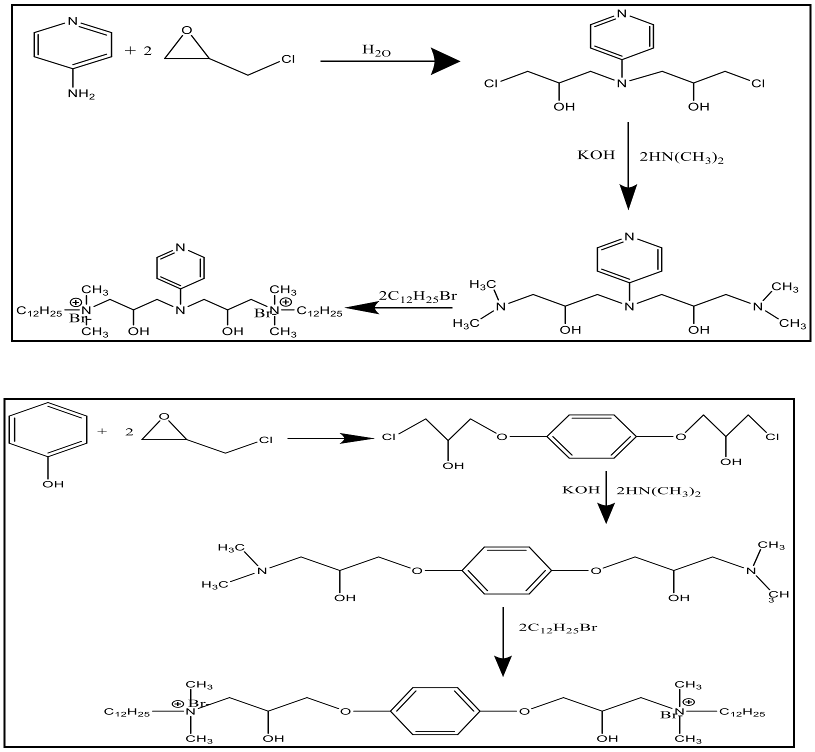
FTIR (NaCl): 3564.45, 3417-3406, 3097.68-3047.53, 2991.59-2933.73, 2962.66- 2935.66, 1772.58-1726.29, 1645.28-1568.13, 1467.83-1408.04, 1392.61-1319.31, 1309.67, 1097.50-1043.49 , 738.74-715.59 cm^{-1}, as shown in Figure 2

^{1}H-NMR (400MHz, DMSO): δ ppm = 0.930-0.880 (t, 6H, 13, 13*), 1.2 -1.4 (m, 36 (12, 12*), 1.7-1.6 (qui, 4H) 2, 2*), 3-3.5 (s,12H) 1, 1*, 4, 4*, 14 , 14*, 15 , 15*), 4.2-3.85 (d, 4H) 6, 6*), 5-4.6 (qui, 2H) 5, 5*), 5.5 (s, 2H, OH) 7, 7*), 8.3-6.8 (d, 4H) 10, 10*, 11, 11*), as shown in Figure 3

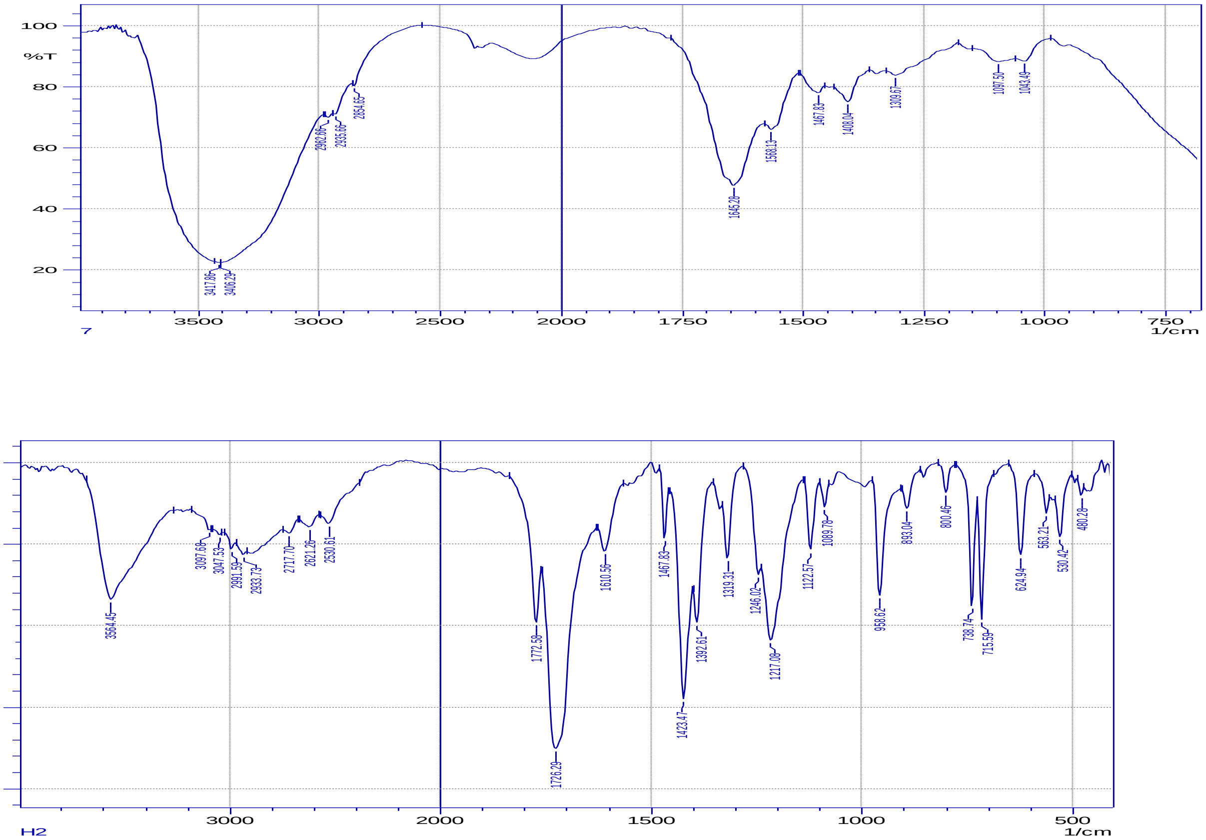
^{1}H-NMR (400MHz, DMSO): δ ppm = 0.92 (t, 6H, 12, 12*), 1.2 -1.4 (m, 36 (11, 11*), 1.8-1.6 (qui, 4H) 2, 2*), 3-3.5 (m, 20H) 1, 1*, 4, 4*, 9 , 9*, 10 , 10*), 4.4-4 (d, 4H) 6, 6*), 5.1-4.7 (qui, 2H) 5, 5*), 5.55 (s, 2H, OH) 7, 7*), 7.5-6.8 (m, 4H) 13, 14, 15, 16) as shown in Figure 3

MS1

MS2



Scheme (1): Methods for preparing MS1 and MS2

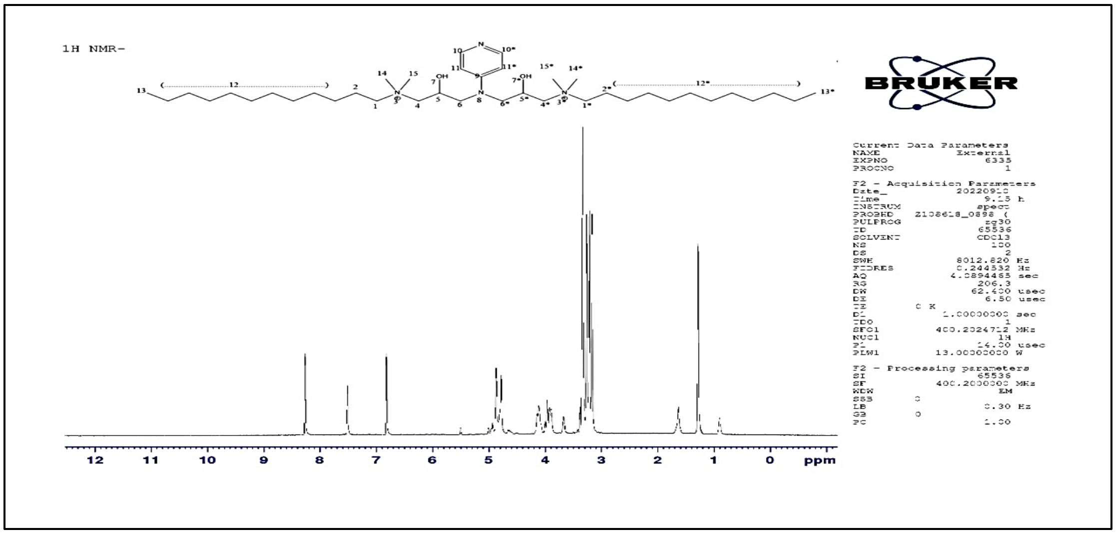


MS1

MS2

Figure (1): FTIR Spectra of MS1 and MS2

MS1



MS2

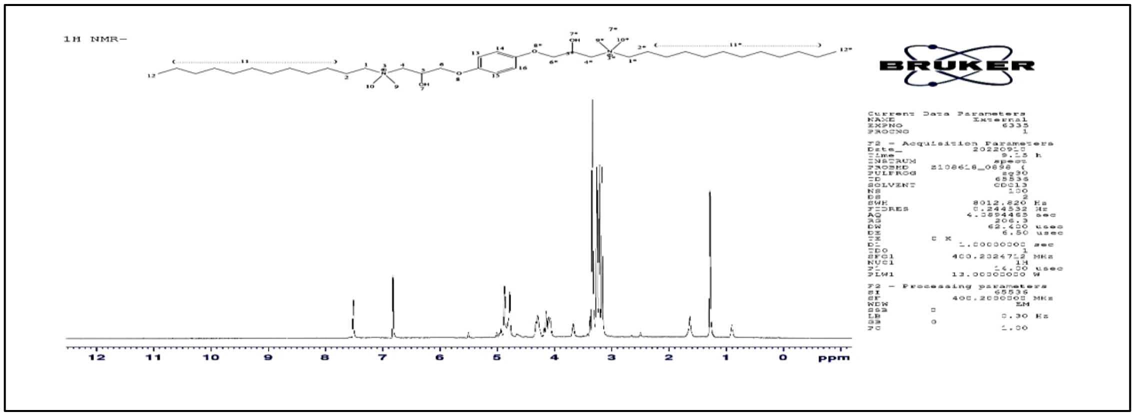


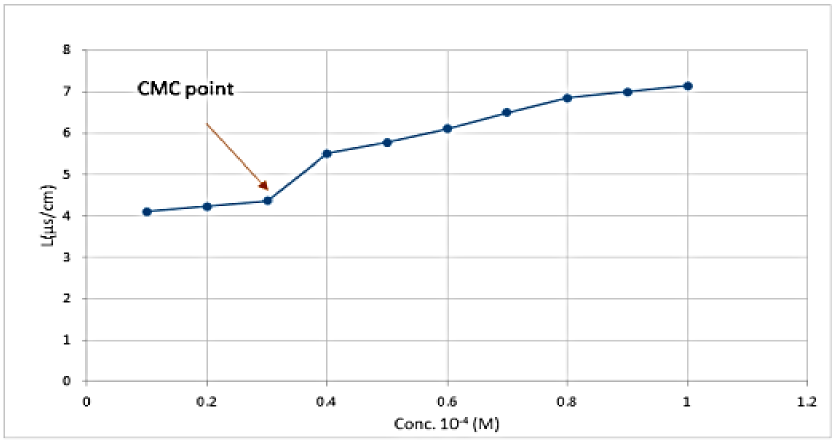
Figure (2): ^{1}H-NMR Spectra of MS1 and MS2

1. Results and Discussion:

3.1- Measurement of CMC Values of Surfactant Solutions by Electrical Conductivity:

The critical micelle concentration CMC of a surfactant is an important physical parameter [20, 21], which can determine it's by the change in the electrical conductance of aqueous ionic surfactant solutions due to cationic ions and anionic ions [22, 23]. The electrical conductivity is usually influenced by solvent and temperature [24, 25] so that have been prepared a series of aqueous solutions of cationic gemini surfactants then measured their conductivity at 25°C. The values of CMC were calculated as the intersection of linear parts in the dependence conductivity versus surfactant concentration [26], and can be observed conductivity change linearly (extrusive) with the change of concentration due to the nature and concentration of counter. Where noted from Figures that impairment of conductivity with reduced concentration of gemini surfactants, can be attributed to a decline in the number of ions that contribute to the electrical conductivity, which leads to lower it, until a specific point is CMC point then be a simple change in the line as shown in the Figure 3**.** We noticed that the CMC value of dispersion MS1 (0.3x10^{-4}M) is less than the value of MS2 (0.6x10^{-4}M). The reason for this is attributed to presence of the heterogeneous ring, which reduces the distance between the two ends of the activated substance and thus increases the process of agglomeration of the molecules and brings them together mor easily, in addition to the presence of the electronic double of the nitrogen atom, which increases from the polarity of the groups and makes it more attractive compared to the aromatic separator present in the MS2 dispersion. The lower the CMC value, the more effective the molecule is, in addition to presence of long hydrocarbon chain that works to lower the CMC value [28].

MS1



MS2

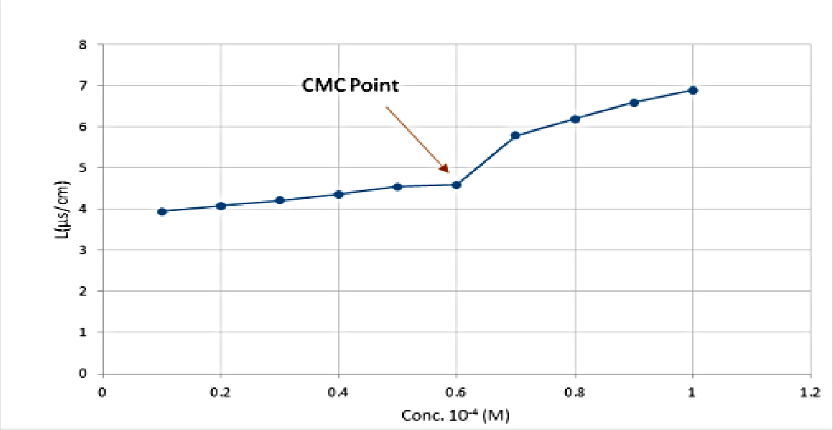
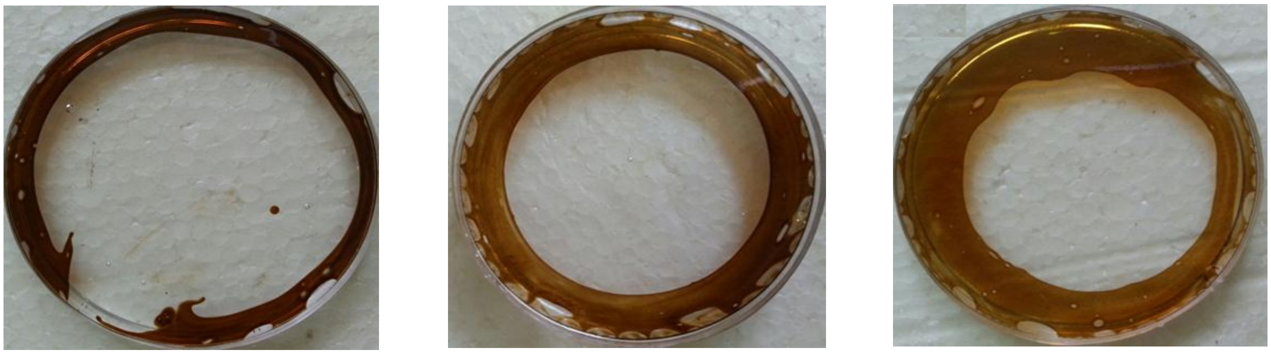


Figure (3): CMC values for MS1 and MS2 dispersions

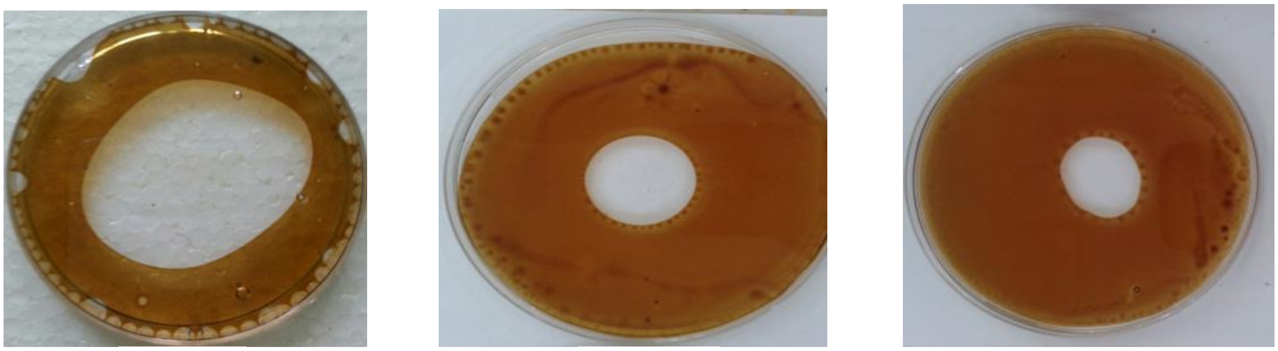
3.2- Study of the Efficiency of Gemini Surfactants as Dispersants:

The dispersions were tested by adding 25mL of water to the test plate and then adding 10μL of oil and remaining for a short period until the situation stabilized. Then add 10μl of the dispersion MS1 and MS2. Where we notice the spread of oil and be a white spot resulting from the penetration of the dispersion wall between water and oil. That the solvent that was selected in the preparation of dispersants is an ethylene glycol, a compound used in the food and pharmaceutical industries and that it is better than water in the industry of dispersants. The study showed that the compound MS1 has greater effectiveness of dispersion of oil from the compound MS2 because of the it contains a separator consisting of a heterogeneous ring containing nitrogen, which increases the dispersion action in order to increase the affinity of compound and the ease of agglomeration and assembly, which leads to a reduction in the CMC value, and thus the dispersibility of the MS1dispersion increases compared to the MS2 dispersion, which it contains a solid separator that hinders the rapprochement between the compound molecules, which leads to an increase in the CMC value, which leads to a reduction in the dispersion action, as shown in Figure 4 [28].



40ppm **30ppm** **20ppm**

MS1



40ppm **30ppm** **20ppm**

MS2

Figure (4): Dispersing the oil-in-water emulsion with different concentration and using MS1 and MS2

The HLB value for MS1 and MS2 was also calculated using Craven equation in order to determine the appropriate application for them, as the values for MS1=6.00 and for MS2= 6.24, which can be used in the treatment of oil-in-water (O/W) and water-in-oil (W/O) emulsions [29].

$$\mathbf{HLB = 20mh / M \;....(1)}$$

Where:

mh: Molecular weight of the hydrophilic end.

M: Total micelle weight.

4. Conclusion:

During the study, it was noted that concentration of 40 ppm for MS1 had a higher oil dispersibility than the concentration of 40 ppm for MS2. It was also noted that the CMC value for MS1 is less than MS2. The reason for this is attributed to the presence of heterogeneous ring, which works to bring the two ends of the compound closer together and facilitates its agglomeration, which increases the action of quenching, in addition to the length of the hydrocarbon chain, which plays a major role in dissolving in oil, which facilitates the process of dispersing oil from water. Unlike MS2 which contains a solid separator that increases the spacing of the molecules and reduces their agglomeration, thus CMC value is higher despite the presence of the same hydrocarbon chain.

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المستخلص:

في البحث الحالي تم تحضير نوعين من منشطات السطوح التوأمية الكاتأيونية الجديدة ذات الفواصل المختلفة (أروماتية وحلقية غير متجانسة) مشتقة من الايبي كلوروهايدرين. شخصت المركبات المحضرة باستخدام مطيافية الاشعة تحت الحمراء FTIR ومطيافية الرنين النووي المغناطيس ^{1}H-NMR . بعدها تم حساب التركيز الغروي الحرج CMC باستخدام التوصيلية الكهربائية وبتحضير سلسلة من التراكيز المولارية لمنشطات السطوح الجديدة فضلاً عن حساب قيمة الموازنة بين المجاميع المحبة للماء والكارهة للماء (المحبة للدهون) HLB. تم تحضير محاليل من منشطات السطوح التوأمية الكاتأيونية بتراكيز مختلفة 20-40 ppm من خلال تحضير اطباق لمستحلبات النفط في الماء لمعرفة كفاءة التشتيت لها حيث لوحظ بأن المادة المشتتة الحاوية على حلقة غير متجانسة MS1 تكون اكثر كفاءة تشتيت من المادة المشتتة الحاوية على حلقة اروماتية MS2 بوجود نفس السلسلة الهيدروكاربونية وعند التركيز 40 ppm.