

Applied Cationic Gemini Surfactant As demulsifier For Breaking Of Water-In-Crude Oil Emulsions

Dalal Hameed Abdalrazzaq

Abstract— Cationic Gemini surfactant A synthesized and characterized by FT – IR , H^1 NMR. The surface properties of the Gemini surfactants were investigated by means of electrical conductivity measurements (determine critical micelles concentration CMC) and obtained the surface tension at CMC point. The results indicated that A and B have superior surface activity. Cationic Gemini surfactants were used to treat the water in oil emulsions and study the effect of heat and setting time on the separation efficiency of water from crude oil.

Index Terms—Cationic Gemini surfactants, Heavy crude oil, critical micelle concentration, Water in oil emulsion.

I. INTRODUCTION

Recently new types of surfactant called Gemini surfactants attracted increasing attention from both industrial and academic fields. Gemini surfactants, which consist of two conventional surfactants joined by a spacer at the head group, as they exhibit significant surface activity properties that cannot be achieved by conventional surfactants [1], [2], [3]. Most studies, however reported on the surface tension of the aqueous solutions of dimeric surfactants for (CMC) determination and assessment of their capacity in the reducing the surface tension of water [4], [5], [6]. These surfactants appear to be better in reducing the oil/water interfacial tension, unusual aggregation morphologies, and better wetting, solubilizing, foaming, and antibacterial activities [7], [8]. Cationic surfactants are used for number of stabilization problems and have found many technical applications, such as soil softeners, enhanced oil recovery, cosmetic products and electro-dicoatings, and the stabilization of adhesive polymer latexes [9], [10]. Because of the predominate negatively charged nature of natural colloids and surfaces, cationic surfactants for strong adsorption layers and hydrophobize the surfaces of these materials [11], [12], [13]. Also the presence of two charged sites in a Gemini proposes stronger interaction with the neutral and oppositely charged ionic surfactants than that of the conventional surfactant combinations. However, only limited number of attempts has been made regarding mixed micellization of the Gemini and single chain surfactants [14], [15].

Through numerous studies on the stability of water-in oil emulsion, more light has been shed on the mechanism of emulsion stabilization in the petroleum field. Many researchers now attribute the stability of emulsion to the viscoelastic interfacial film made up of surface active molecules such as asphaltene, resins, and other organic and inorganic particles [16]. The degree to which solids increases

emulsion stability depends on several factors such as particle size, shape and morphology, density, concentration and surface coverage, and wettability [17], [18], [19], [20], [21], [22]. There is a strong correlation between asphaltene content and emulsion tightness [23]. The presence of wax in addition to asphaltene and resins are known to promote the stabilization of water-in-oil emulsion. Asphaltenes are flat sheets of condensed polyaromatic hydrocarbons linked together by sulfide, ether, and aliphatic chain groups. The edges of the sheets are alkyl chains. The polar parts of the asphaltene molecules interact with each others forming aggregates or micelles. As such, these micelles are very much polar. Resins are less polar and made up of smaller molecules with one end being hydrophilic made up of functional groups and the other end hydrophobic made up of alkyl chains. In crude oils, the resins are attached to the asphaltene micelles at the polar end and the non polar end of the resin interact with crude oil. The resins solvate the asphaltene aggregates and keep them in colloidal suspension in the oil [24].

In these investigations, we have applied quaternary ammonium Gemini surfactants with hydroxyl groups as demulsifier to treat the emulsions of water in oil (W/O) in different type of crude oil [25], [26], [27].

II. EXPERIMENTAL

2.1. Materials and instruments

The following materials purchased from different companies: Propylene glycol (99.5 % purity), Sodium hydrogen sulfate (98% purity), Epichlorohydrin (98.5% purity), petroleum etherdist. (ASTM D86-87) between 40 and 60°C (98% purity), ethyl acetate (99% purity), Potassium hydroxide (99% purity), 33% aqueous dimethyl amine, chloroform(99% purity), anhydrous magnesium sulfate (99.5 % purity), methanol (99.8 % purity), 1-bromo tetra decane (98 % purity), absolute isopropyl alcohol (99.7 % purity), silica gel high-purity grade 40 (35-70 mesh). Twice distilled water was used in the preparation of all solutions.

1H NMR spectra was recorded on a Bruker AM 500 spectrometer. $CDCl_3$ was used as solvent and chemical shifts recorded were internally referenced to TMS (0 ppm). IR spectra were obtained on a Thermo Electron Corporation Nicolet 380 FT-IR spectrophotometer. Thin layer chromatography (TLC) was conducted on silica gel uniplates, and The CMC values of the surfactant solution were determined from Electrical conductivity with a WTW Inolabcond 740 conductivity meter (Germany).

2.2. Synthesis of Cationic Gemini surfactants

2.2.1. Synthesis of Gemini surfactants A

There are three steps to get the target compound A:

Dalal Hameed Abdalrazzaq , Chemistry Department, General Director of Education, Al- Kalisah secondary school / Basrah, Iraq, 009647815553106.

1. Compound

/3,3'-(propane-1,3-diylbis(oxy))bis(1-chloropropan-2-ol).

To a mixture consisting of Propylene glycol (22.8 g, 0.3 mol), Sodium hydrogen sulfate NaHSO₄ (1 g, 8mmol), water (0.6 mL), added Epichlorohydrin (55.5 g, 0.6 mol) drop wise at 0 °C . The mixture was stirred for 5 hours and heated to 90 -100 °C. After that the mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 1:4, v/v) to give the target compound as transparent oil (yield 83.6 %) [28], [29].

IR (KBr): 3405, 2998, 2875, 1454.9, 1332, 715 cm⁻¹. ¹H NMR (500 MHz, CDCL₃): δPPm= (1.64 – 1.9) OCH₂CH₂CH₂O(m, 2H, CH₂), (3.36 – 3.48)OCH₂CH₂CH₂O (t, 4H, CH₂), (3.55 – 3.67) CH₂O(CH₂)₃OCH₂ (d, 4H, CH₂), (3.86 – 4.02) O(CH₂)₃OCH₂CHOH (m, 2H, CH), (4.22) O(CH₂)₃OCH₂CHOH(s, 2H, OH), (3.68 – 3.76) OCH₂CHOHCH₂Cl (d, 4H, CH₂).

2. Compound/2,14-dimethyl-6,10-dioxo 2,14-diazapentadecane-4,12-diol.

To a flask containing (0.67 g, 12 mmol) Potassium hydroxide was added 33% aqueous dimethyl amine (0.9 g, 0.02 mol) , then added compound which prepared in first step (2.8 g, 0.01 mol) as drop wise with a magnetic stirrer at room temperature to produce precipitate. The mixture was filtered then the filtrate was extracted with chloroform and dried over anhydrous magnesium sulfate. After evaporation to remove solvent and the residue was purified by column chromatography on silica gel (methanol/ethyl acetate, 1:5, v/v) to give the target compound as yellow oil (yield 70.14%). IR (KBr): 3430, 2958.20, 2865.23, 1450.5, 1340, 1205, 1103.9 cm⁻¹. ¹H NMR (500 MHz, CDCL₃): δ Ppm = (1.70 – 1.83) OCH₂CH₂CH₂O (m, 2H, CH₂), (3.22 – 3.36) OCH₂CH₂CH₂O (t, 4H, CH₂), (3.48 – 3.51) CH₂O(CH₂)₃OCH₂ (d, 4H, CH₂) , (3.76 – 3.95) O(CH₂)₃OCH₂CHOH (m, 2H, CH), (4.12) O(CH₂)₃OCH₂CHOH (s, 2H, OH), (3.55 – 3.68) OCH₂CHOHCH₂N (d, 4H, CH₂), (2.73) CH₂N(CH₃)₂ (s, 12H, CH₃) .

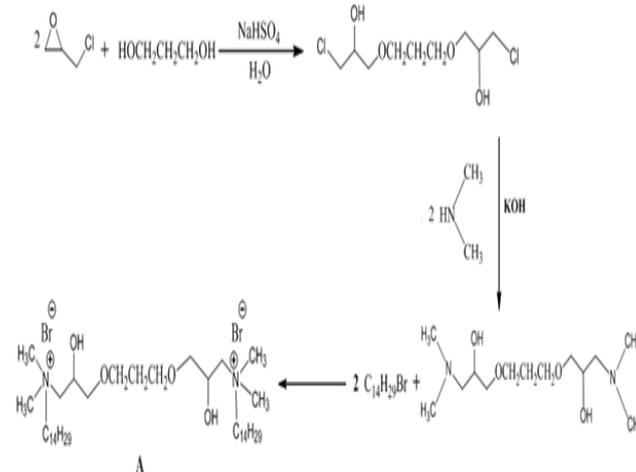
3. Compound A/

N,N'-(propane-1,3-diylbis(oxy))bis(2-hydroxypropane-3,1-diyl)bis(N,N-dimethyltetradecan-1-aminium) dibromide

To a flask containing 1-bromo tetra decane (2.00 g, 7.19mmol) and absolute isopropyl alcohol (50 mL) was added compound which prepared in second step (1.0 g, 3.6mmol) at room temperature. The mixture was refluxed for 1 hour. After reaction the mixture was subjected to evaporation and the residue was purified by column chromatography on silica gel (methanol/ethyl acetate, 1:5, v/v) to give the target compound (A) as yellow oil (yield 76.9 %).The structure and synthetic route of this surfactant is shown in Scheme 1.

IR (KBr): 3450.69, 2967.33, 2875.23, 1454.33, 1350.13, 1253.73, 1107.23 cm⁻¹. ¹H NMR (500 MHz, CDCL₃): δ Ppm = (1.9 – 2.17) OCH₂CH₂CH₂O (m, 2H, CH₂); (4.2– 4.3) OCH₂CH₂CH₂O (t, 4H, CH₂) ; (4.02 – 4.15) CH₂O(CH₂)₃OCH₂ (d, 4H, CH₂) ; (4.4 – 4.62) O(CH₂)₃OCH₂CHOH (m, 2H, CH) ; (3.9) O(CH₂)₃OCH₂CHOH (s, 2H, OH) ; (3.2 – 3.29) OCH₂CHOHCH₂N (d, 4H, CH₂) ; (3.09) CH₂N(CH₃)₂ (s,

12H, CH₃) ; (3.3 – 3.49) N(CH₃)₂CH₂(C₁₃H₂₇) (t, 4H, CH₂) ; (1.59 – 1.81) N(CH₃)₂CH₂CH₂(C₁₂H₂₅) (m, 4H, CH₂); (1.18 – 1.49) CH₂CH₂(CH₂)₁₀CH₂CH₃ (m, 40H, CH₂) ; (0.82 – 1.03) CH₂(CH₂)₁₀CH₂CH₃ (m, 4H, CH₂) ; (0.5 – 0.74) CH₂(CH₂)₁₀CH₂CH₃ (t, 6H, CH₃).



Scheme 1.Synthetic route to Gemini surfactant A

III. RESULTS AND DISCUSSION

3.1. Measurement of CMC Values

The critical micelle concentration (CMC) of a surfactant is an important physical parameter [30], [31], which can determine it's by the change in the electrical conductance of aqueous surfactant solutions and this method can only be applied to measure the CMC of ionic surfactants. [32], [33]. The electrical conductivity is usually influenced by solvent and temperature [34], [35] so that have been prepared a series of aqueous solutions of Gemini surfactants then measured their conductivity at 25 °C.

Where noted from Figure (1) that impairment of conductivity with reduced concentration of Gemini surfactants, can be attributed to a decline in the electrical conductivity, until a specific point is CMC point. In addition Gemini surfactants from epichlorohydrin exhibit large intermolecular hydrophobic interactions that make it easy for them to form aggregates in water [36]. Compounds with small polar heads are influenced by the length of the aliphatic tail to a much greater extent than surfactants with large non-ionic polar-regions. The ionic quaternary compound A tested show the CMC values at (1.7 x 10⁻⁴ M) (Fig. 1).

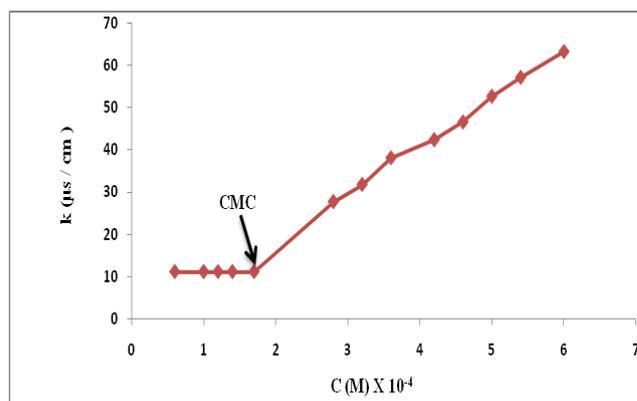


Figure 1. CMC of cationic dimeric surfactants A

3.2. Study the Efficiency of Gemini Surfactants as Demulsifier

Demulsifier of the most important factors affecting the separation efficiency of water from oil, and to allow the mixed phases to be separated from each other, where the separation efficiency of emulsions depend on structure of Gemini surfactant and additives used in the composition of demulsifier. The separation efficiency of water from crude oil can be calculated from equation (1) [37].

$$\% E_{\text{Separation}} = (V_S / V_T) \times 100 \dots\dots (1)$$

Where:

$\% E_{\text{Separation}}$: The percentage of separation efficiency of water from crude oil.

V_S : Volume of water separated (ml).

V_T : Total volume of brine (15 ml) in crude oil.

The crude oils applied as model in this study were heavy and light. Specifications and some physical and chemical properties of these crude oils are listed in table 1.

Table 1: Physicochemical properties of the crude oils

Characteristics	Method	Light crude oil	Heavy crude oil
Specific Gravity @ 60 °F	IP160	0.8280	0.9293
API Gravity	IP160	39.4	20.8
Sulphur Content , wt. %	ASTM D-4294	1.00	3.30
Asphaltenes , wt. %	IP-143	< 0.05	9.6
Kinematic Viscosity , cSt.	IP-71	4.101	112.0
		2.986	52.50
		2.501	32.47
		2.102	22.50

The industrial emulsion was prepared by mixing constant volume from 15% brine water (200,000 ppm) with 85 % crude oil to become the overall percentage 100 %. Emulsion was Distributed in glass tubes (capacity tube 100 cm³) and placed one of them in a water bath at 25 C° and read water separated (five readouts).

The demulsifier which prepared from compound a was studied with light crude oil. As shown in table (2), it can be noted that at the temperature 25°C, the percentage of the best separation efficiency ($\% e_{\text{separation}}$) was (93.3 %) in concentration 30 ppm .

Table 2: The volume of separated water when used the demulsifier which prepared from compound A with light crude oil

Dosage ppm	Separated Water (ml)					% E Separation
	After 10 min.	After 30 min.	After 60 min.	After 90 min.	After 120 min.	
10	0.8	2.0	4.0	8.0	10.0	66.7
20	2.5	5.0	7.5	11.0	12.0	80.0
30	4.0	6.0	8.0	11.0	14.0	93.3
40	5.5	7.5	9.5	12.0	14.0	93.3
50	7.0	9.0	13.0	14.0	14.0	93.3

Finally, the demulsifier was studied on heavy crude oil. As shown in Table (3), it can be noted that the percentages of

the best ($\% E_{\text{Separation}}$) was (43.3 %), respectively in concentration 40 ppm.

Table 3: The volume of separated water when used the demulsifier which prepared from compound A with heavy crude oil

Dosage ppm	Separated Water (ml)					% E Separation
	After 10 min.	After 30 min.	After 60 min.	After 90 min.	After 120 min.	
10	Nil	Trace	1.0	3.0	4.5	30.0
20	Trace	0.8	2.0	4.0	5.0	33.3
30	0.6	1.5	3.0	5.0	6.0	40.0
40	2.0	2.5	4.0	5.5	6.5	43.3
50	2.8	3.5	5.0	6.5	6.5	43.3

Water separation efficiency of the demulsifier after 120 minutes for each crude oil that has been used are compared with each other, as shown in Figure (2) where the separation efficiency at both temperatures is as follows:

Light Crude Oil > Heavy Crude Oil

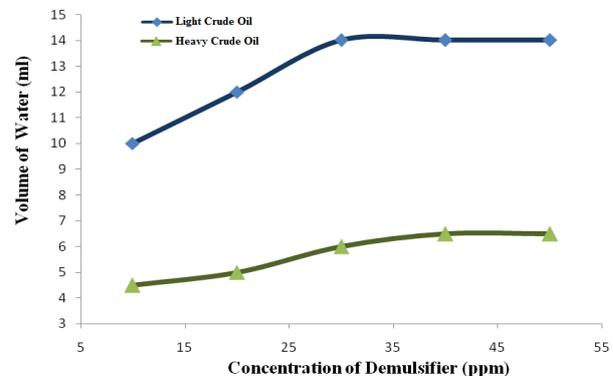


Figure 2. Effects of the Demulsifier on Different Types of Crude Oils

Petroleum emulsions of the W/O variety are almost exclusively stabilized by Asphaltenes. Through the results, it is found that the primary reason of asphaltene stabilization of W/O emulsions is through the formation of a viscous, crosslinked three - dimensional network with high mechanical rigidity. The forces of crosslink asphaltenic molecules at oil – water interfaces are likely much stronger than simple dispersion forces due to hydrogen bonds or electron donor – acceptor interactions. Therefore, Light crude oil is an easy treatment of emulsions that have been formed in it because it has low asphaltene content (< 0.05 %) making the separation efficiency is high. While Heavy crude oil has the worst separation efficiency due to high asphaltene content (9.6%).

There are several salient features to asphaltene for stabilizing films. First, surface adsorption of asphaltene molecules is probably driven by hydration of polar functional groups in the aromatic core of an individual asphaltene molecule. Second, resin molecules probably serve to solvate primary aggregates in the bulk phase, but these resins are likely shed and do not appreciably participate in the actual stabilizing film. In fact, the resins are totally unnecessary in the stabilization of asphaltenic films.

IV. CONCLUSION

Generally, emulsion breaking occurred by supplied demulsifiers, where water separation efficiency increases with increasing dosage of prepared demulsifiers. Water separation

efficiency increases with increasing separation time for all types of demulsifiers, where maximum separation obtained is at (120min). Also, the prepared demulsifier has good efficiency at light crude oil that has low asphaltene content because petroleum emulsions of the W/O are stabilized by asphaltenes. Therefore, water separation efficiency increases with decrease asphaltene content.

V. ACKNOWLEDGMENT

Finally, I would like to express my sincere thanks to Dr. Najlaa Z. Alameri, who is working in South Oil Company for help us to achieve our research.

REFERENCES

[1] Limei Zhou, Hua Chen, Xiaohui Jiang, Fang Lu, Yafen Zhou, Wenmin Yin, Xiaoyang Ji, Modification of montmorillonite surfaces using a novel class of cationic gemini surfactants, *J. Journal of Colloid and Interface Science* 332 (2009) 16–21.

[2] Hongqi Li, Chaochao Yu, Rui Chen, Juan Li, Jinxing Li, Novel ionic liquid-type Gemini surfactants: Synthesis, surface property and antimicrobial activity, *J. Colloids and Surfaces A: Physicochem. Eng. Aspects* 395 (2012) 116–124.

[3] Dipti Shukla, V.K. Tyagi, Cationic Gemini surfactants: A review, *J. Oleo Sci.*, Vol. 55, No.8, (2006) 381-390.

[4] F. Devinsky, L. Masarova and I. Lacko, Surface activity and micelle formation of some new Bis- quaternary ammonium salts, *J. Colloid interface science*, Vol. 105, 235-238 (1985).

[5] F. Devinsky and I. Lacko, Surface activity and micelle formation of some new Bis- quaternary ammonium salts of glycerine derivative, *J. Tenside surf. Deterg.*, Vol. 27, 334-349 (1990).

[6] F. Devinsky, I. Lacko, F. B. Bitterova and L. Tomeckova, Relationship between structure, surface activity, and micelle formation of some new Bis- quaternary isosteres of 1,5-pentanediammonium dibromides, *J. Colloid interface science*, Vol. 114, 314-322 (1986).

[7] G. RoshanDeen, L.H. Gan, Y.Y. Gan, A new cationic surfactant N,N'-dimethyl-N-acryloyloxyundecylpiperazinium bromide and its PH-sensitive gels by microemulsion polymerization, *J. Polymer* 45 (2004) 5483–5490.

[8] Drew Myers, *Surfactant science and technology*, Third edition, 2006.

[9] Fang Yang, Gang Li, Nian Xu, Rong Liu, Song-Mei Zhang, Zeng-Jiang Wu, Synthesis and Critical Micelle Concentration of a Series of Gemini AlkylphenolPolyoxyethylene Nonionic Surfactants, *J. SurfactDeterg* (2011) 14:339–345.

[10] Laurier L. Schramm, *Surfactants: Fundamentals and Applications in the petroleum industry*, first published 2000.

[11] Bo Cai, Xuefeng Li, Yi Yang, Jinfeng Dong, Surface properties of Gemini surfactants with pyrrolidinium head groups, *J. Colloid and Interface Science* 370 (2012) 111–116.

[12] Jia Wei, Guohe Huang, Hui Yu, Chunjiang An, Efficiency of single and mixed Gemini/conventional micelles on solubilization of phenanthrene, *J. Chemical Engineering Journal* 168 (2011) 201–207.

[13] Richard J. Farn, *Chemistry and Technology of Surfactants*, published 2006.

[14] MohamadShafi Sheikh, Kabir-ud-Din, Aijaz Ahmad Dar, Synergistic interaction of Gemini surfactant pentanediyl-1,5-bis(dimethylcetylammmonium bromide) with conventional (ionic and nonionic) surfactants and its impact on the solubilization, *J. Colloids and Surfaces A: Physicochem. Eng. Aspects* 378 (2011) 60–66.

[15] Qi Zhang, Zhinong Gao, Feng Xu, Shuxin Tai, Effect of hydrocarbon structure of the headgroup on the thermodynamic properties of micellization of cationic gemini surfactants: An electrical conductivity study, *J. Colloid and Interface Science* 371 (2012) 73–81.

[16] Sullivan, A.P. and Kilpatrick, P.K. (2002) *Ind. Eng. Chem. Res.*, 41: 2289–3404.

[17] Gelot, A., W. Friesen, W., and Hamza, H.A. (1984) *Colloids Surf.*, 12: 271–303.

[18] Yan, Z., Elliott, J.A. W., and Masliyah, J.H. (1999) *J. Colloid Interface Sci.*, 220: 329–337.

[19] Yan, N., Gray, M.R., and Masliyah, J.H. (2001) *Colloids Surfaces A*, 193: 97–107.

[20] Tambe, D.E. and Sharma, M.M. (1993) *J. Colloid Interface Sci.*, 157: 244–253.

[21] Tambe, D. E. and Sharma, M.M. (1994) *J. Colloid Interface Sci.*, 162: 1–10.

[22] Aveyard, R., Binks, B.P., and Clin, J.H. (2003) *Adv. Colloid Interface Sci.*, 100–102: 503–546.

[23] Kokal, S. and Wingrove, M. (2000) Emulsion separation index: from laboratory to field cases. Paper SPE 63165. Proceedings of the SPE Annual Technical Conference and Exhibition, Dallas, TX, USA, October.

[24] Adel M. Elsharkawy, Taher A. Al-Sahhaf, and Mohammed A. Fahim: *J. Dispersion Science and Technology*, Vol. 33, No. 1, (2012) 805–811.

[25] G. R. Deen, L.H. Gan and Y.Y. Gan: (2004), A new cationic surfactant N,N'-dimethyl-N-acryloyloxyundecyl piperazinium bromide and its pH-sensitive gels by microemulsion polymerization, *J. Polymer*, 45: 5483–5490.

[26] J. Wei, G. Huang, H. Yu and C. An: (2011), Efficiency of single and mixed Gemini/conventional micelles on solubilization of phenanthrene, *J. Chemical Engineering*, 168: 201–207.

[27] Q. Zhang, Z. Gao, F. Xu and X. Zou: (2011), Adsorption and corrosion inhibitive properties of gemini surfactants in the series of hexanediyl-1,6-bis-(diethyl alkyl ammonium bromide) on aluminium in hydrochloric acid solution, *J. Colloids and Surfaces A: Physicochem. Eng. Aspects*, 380: 191–200.

[28] D. L. Rahmankulof, B. K. Kemcanof, N. A. Lokmeonof, U. K. Dmumreef, R. R. Chaneshef, Epichlorohydrin, synthesis procedure, physical and chemical properties, production technology, Moscow chemistry 2003.

1)

2) [29] G. A. Akmedova, *New Oligomer surfactants from ethylene glycol and epichlorohydrin*, *J. Applied chemistry*. 2008. T. 81.

[30] H. Akbas, A. Elemenli and M. Boz: (2012), Aggregation and Thermodynamic Properties of Some Cationic Gemini Surfactants, *J. Surfact Deterg*, 15: 33–40.

[31] Richard J. Farn: (2006), *Chemistry and Technology of Surfactants*, Published by Blackwell Publishing Ltd, Oxford, UK.

[32] Q. Zhang, Z. Gao, F. Xu and S. Tai: (2012), Effect of hydrocarbon structure of the headgroup on the thermodynamic properties of micellization of cationic gemini surfactants: An electrical conductivity study, *J. Colloid and Interface Science*, 371: 73–81.

[33] T. Lu, Y. Lan, C. Liu, J. Huang and Y. Wang: (2012), Surface properties, aggregation behavior and micellization thermodynamics of a class of gemini surfactants with ethyl ammonium headgroups, *J. Colloid and Interface Science*, 371: 1–9.

[34] A. Dominguez, A. Fernandez, N. Gonzalez, E. Iglesias and L. Montenegro: (1997), Determination of Critical Micelle Concentration of Some Surfactants by Three Techniques, *J. Chemical Education*, 74: 1227 – 1231.

[35] A. Kroflic, B. Sarac and M. B. Rogac: (2012), What Affects the Degree of Micelle Ionization: Conductivity Study of Alkyltrimethylammonium Chlorides, *J. Acta Chim. Slov.*, 59: 564–570.

[36] M. S. Sheikh, K. Din and A. A. Dar: (2011), Synergistic interaction of Gemini surfactant pentanediyl-1,5-bis(dimethylcetylammmonium bromide) with conventional (ionic and nonionic) surfactants and its impact on the solubilization, *J. Colloids and Surfaces A: Physicochem. Eng. Aspects*, 378: 60–66.

[37] Najlaa Z. Rajab: (2014), Ph. D Thesis, University of Basra, Iraq.

Dalal Hameed Abdalrazzaq completed her graduation in chemistry (2005) at the University of Basrah, Iraq. After that, she began her M.Sc. studies in 2012 under the guidance of Dr. Muhanned J. Al-Assadi, at Chemistry Department, College of Education for Pure Sciences, University of Basrah, Iraq.