

Preparation of de-emulsifier of Gemini surfactant and it's applications in an oil industry

Georgius A. Adam^(a), Nazar A. Hussein^(b), Zaydoon K. Kreamid^(c)

a: University of Sydney, Australia, b: College of Education, university of Basrah .

c: Ministry of oil / Oil products distribution Company .

Abstract:

A Gemini surfactants(GS) is a bis quaternary amonium salt.It is prepared from tetramethyl ethylene diamine(TMEDA)with cetyl bromide, while an ordinary surfactant(OS), which is quaternary ammonium salt, is prepared from trimethyl amine(TMA) and cetyl bromide. They were identified by elemental analysis and IR spectroscopy.

Comparing the GS, OS and the commercial surfactants, the Gemini surfactant shows an interesting properties and have a variety of of uses, such as a de - emulsifier.

Adopting the composition ratios found in the study of reverse chemistry of commercial de-emulsifier, Rp6000, which is usually use in the south and north oil companies in Iraq. The prepared active reagent were characterized by various techniques, IR spectroscopy, elemental analysis, melting point, solubility, flash point and functional group analysis.

The efficiency of the prepared de-emulsifier was examined by standard methods and compared with the efficiency of the commercial Rp6000 based on the same wet crude oil sources .

Introduction:

Emulsions are unstable thermodynamic systems which contain two immisible liquid phases. The emulsion causes many problems such as corrosion, or effect the quality and

properties of oil. One of the methods of treatment of this problem is by using de-emulsifier (tensider or emulsion breaker) ⁽¹⁾.

These systems can be dissociate in the presence of a kind of surfactants known as

emulsifying agents. These agents consist of two groups, polar(hydrophilic) like aqueous phase and non polar group(hydrophobic) like an oil ⁽²⁾.

Surfactants were known for a long time. They are known for the ancient Egyptians and Babylonians, and they were made of animal fats and plants oil. They were used for detergents, drugs, dyes and many other industries such as emulsifiers and de-emulsifiers ⁽³⁾.

The de-emulsifiers reduce the surface tension for liquids and then dissociate the large oil blocks. It increases the interfacial action ⁽⁴⁾. This activity depends on the nature of surface active material, the molecular weight and the length of the molecular chain

In this work we used a surfactant which can be used in an oil industry as an important economic field. As it is well known, there are two kinds of emulsions in an oil industry , water / oil (w / o) , and oil / water (o / w) ⁽⁵⁾. The difference between them is the nature of the dispersed and continuous phases. Each one has its own method .

The (w / o) emulsion was used to treat the wet crude oil , which is as a result of the injection of water into the oil Wells. To get better efficiency of surfactant, the Gemini surfactant (GS)⁽⁶⁾ was used, which have many hydrophilic groups linked together by spacer ⁽⁷⁾.

Experimental work:

1. Preparation of the compounds:

1- Preparation of cetyl bromide($\text{CH}_3(\text{CH}_2)_{15}\text{Br}$) ⁽⁸⁾:

A mixture of 10 ml(0.043 mole) of cetyl alcohol and 33ml(0.215 mole) of 48% HBr (1:5 mole ratio) was refluxed for 4 hours. The reaction mixture then cooled, and the unreacted cetyl alcohol was extracted with absolute methanol(3 times).

The liquid product then dried with anhydrous MgSO_4 . The cetyl bromide then distilled. The yeild is 75%(9.5 g). bp: 122-124⁰C, mp:16.18⁰C ⁽⁹⁾.

2- Preparation of GS(quaternary ammonium salt):

Tertiary ammonium salt was prepared in two necked round bottomed flask fitted with separating funnel and condenser. A solution of 6.3 ml (0.01mole) of tetramethyl ethylene diamine and 30 ml of dry ethanol as a solvent was placed in the flask. The solution then heated to 50⁰C and then 60.2 ml(0.02 mole) of cetyl bromide was added drop wise by the separating funnel for 60 minutes at 50⁰C. After the addition was completed, the temperature raised to 80⁰C and the reaction was continued for 24 hours. The solvent then evaporated by rotary evaporator.

The product is white solid material which was dried and then recrystallised with a mixture of hexane and ethanol(1:1)⁽⁹⁾. The product is soluble in

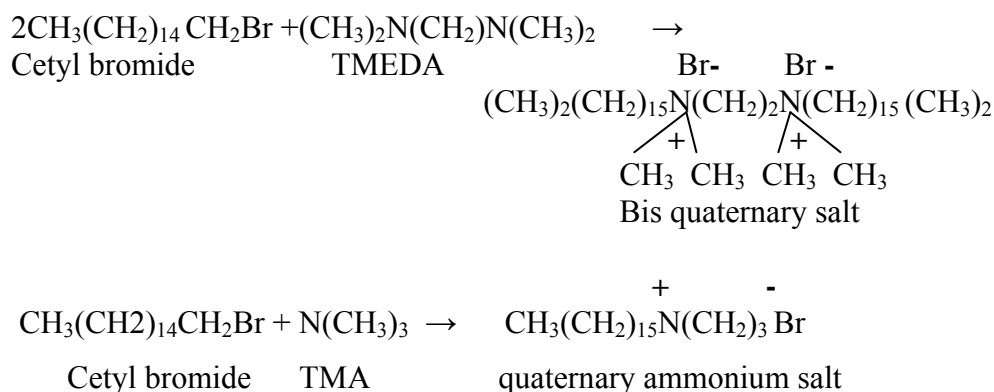
water, xylene and toluene. The yield is 67.5%(50.1g).

3- Preparation of ordinary surfactant (OS):

In three necked rounded bottomed flask fitted with mechanical stirrer, separating funnel and condenser. 11.82g(0.02 mole) of trimethyl amine(TMA) was placed followed by the addition of a solution of

2. Identification of the compounds:

The suggested reaction for the preparation of GS is



The prepared compounds were characterized by CHN analysis:

For GS: Calculated: C=62.61, H=11.616, N=3.844;

Found: C=62.89, H=11.316, N=3.955.

For OS: Calculated: C=62.78, H=11.371, N=3.854,

Found: C=63.01, H=11.213, N=3.975.

The analysis was performed in the Hospital of Hawali, Kuwait.

The IR spectra for GS and OS (figure 1 and 2) show a similarity which is due to the similarity in general structure. The spectra shows the C-N and C-H stretching vibration at 1450 cm⁻¹ and 2980 cm⁻¹ respectively and C-H bending at 1370 cm⁻¹ in addition to CH₂

30.5g(0.01 mole) of cetyl bromide in 50 ml of xylene by the separating funnel was dropwised with stirring for 9 hours at 105⁰C. The heating was in an oil bath.

The white solid product then recrystallised from ethyl acetate.

Decomposition temperature is 251⁰C. The yield is 53.6%(19.5g).

The prepared compounds were characterized by CHN analysis:

For GS: Calculated: C=62.61, H=11.616, N=3.844;

Found: C=62.89, H=11.316, N=3.955.

For OS: Calculated: C=62.78, H=11.371, N=3.854,

Found: C=63.01, H=11.213, N=3.975.

The analysis was performed in the Hospital of Hawali, Kuwait.

The IR spectra for GS and OS (figure 1 and 2) show a similarity which is due to the similarity in general structure. The spectra shows the C-N and C-H stretching vibration at 1450 cm⁻¹ and 2980 cm⁻¹ respectively and C-H bending at 1370 cm⁻¹ in addition to CH₂

bending vibration for the rest of aliphatic chain at 730 cm⁻¹. The spectra were performed by Shimadzu FT-IR-8400s in the petrochemical company, Basrah, Iraq.

3. Reverse chemistry and analysis of commercial surfactant of trade mark Rp6000 .

Due to the importance of the Rp6000 as w/o de-emulsifier, it was analyzed using reverse chemistry method . 100 ml of Rp6000

where distilled at 163 °C, giving 80 ml solvent and 20 g of solid residue. Comparing the boiling point of the solvent with the literature shows that it is similar to Mesitylene(bp:163-164). The analysis results where shown in tables 1 and 2 .

Table (1) : The results of the reverse chemistry of Rp 6000 .

compound	Refractive Index	Aromaticity test	Sulphur test(qualitative)	Density g/ml	Solid / Liquid g/ml
1,3,5 tri methyl benzene (Mesitylene)	1.49846	+	+	0.8638	20/80
Experimental literature	1.4990			0.8640	

Table (2) : The elemental analysis for the solid residue .

The predicted compound RNHSO ₃ Na (C ₁₇ H ₃₆ NSO ₃ ⁻ Na ⁺)			Calculated		
Found					
C	H	N	C	H	N
60.01	9.915	3.925	58.176	10.308	3.77

IR for solid residue, figure (3), shows: C-H: stretching vibration 2980 cm⁻¹, C-H: bending vibration 1380 cm⁻¹, N-H: stretching vibration 3490 cm⁻¹; S=O, stretching vibration 1250 cm⁻¹, N -S: stretching vibration 1220 cm⁻¹ .

4. Preparation of de-emulsifiers :

A : Preparation of Gemini de-emulsifier (Dgm) .

The Gemini de-emulsifier was prepared by mixing the same structural proportions as it was found for the commercial Rp6000 (20/80 g / ml) : 10 g of GS, 5 g of Benzen sulphonic acide and 5 g of oil type (50 S)⁽⁷⁾, 75 ml of a solvent mixture of (Toluene , Xylene, 2/1,v/v , and 5 ml of 1000 ppm of AgNO₃ solution) .

The sulphonic acide was used to increase the viscosity and to reduce the cohesion forces between the immiscible phases. AgNO_3 solution was used in order to increasing the efficiency of separation⁽⁵⁾.

B : Preparation of convensional de-emulsifier (Dos) .

The Dos was prepared following the same procedure for (GS) by introducing ordinary surfactant (OS) in stead of the GS⁽⁷⁾.

5. The physical properties of the de-emulsifiers :

Some of the physical properties of Dgs , Dos and Rp6000 as measured experimentally are shown in table (3) bellow, The measurements where taken at 25⁰C

:

Table (3) : shown a similarity in them physical properties .

The material	Density g/ml	Viscosity (centipois)	Refractive index	PH	Flash point ° C
Rp6000	0.877	1.4905	1.50117	5.8	57
Dos	0.8767	1.4896	1.500087	5.8	55
Dgs	0.8920	1.4899	1.5267	5.8	61

6. Application of surfactant:

The prepared surfactants were applied for two types of (w/o) sample mixtures (high proportion and low proportions of water) .

The first samples were taken from northern and southern Fekka (FQ_n, FQ_s) which are belong to Meisan oil fields, which have large proportions of water. The second sample were taken from Bazirgan oil fields which have low proportions of water (25 %) .

The oil of low proportion of water (second type) was separated using a high concentration of commercial de-emulsifier

(Rp6000) to get it dry , which then mixed with water of a proportion of 10% (w/o) in a test tube with a continuous stirring for one hour. The testing de-emulsifier concentration was in the range 20–50 µg/ml of Dgm, Dom and Rp6000 respectively to the volume of the emulsion .

The results were compared with blank samples which were all left for 30 minutes in a water bath at 50⁰C. The temperature of 50⁰C was taken as an everage of the operating temperature range of 40-60⁰C in an oil companies in Iraq⁽⁹⁾.

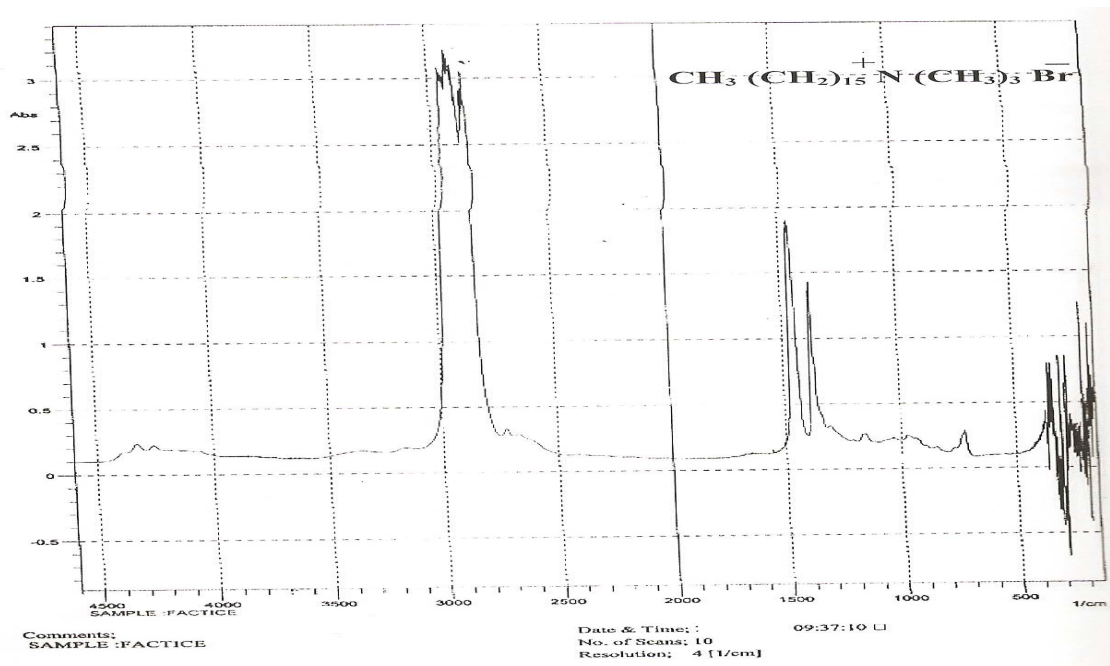


Figure (1): The IR Spectrum of OS

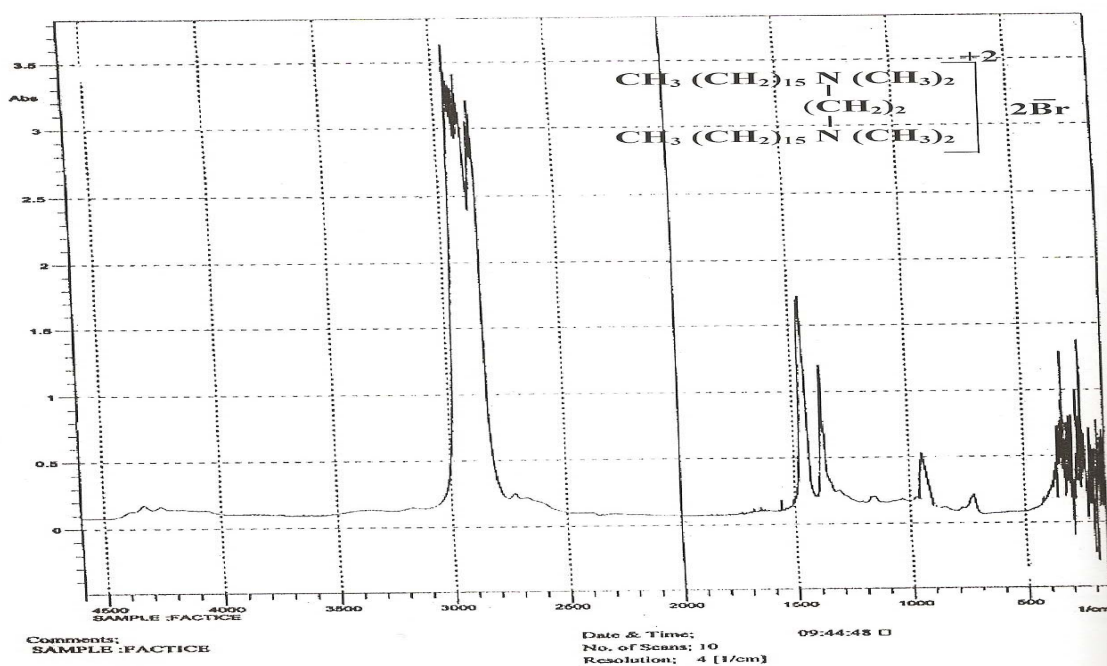


Figure (2): The IR Spectrum of GS

The study shows that the higher concentration for all d-emulsifiers have better separation efficiency, as the temperature reduce the surface tension according to Vonetoves relation⁽¹⁰⁾.

The study shows that Dgs has excellent separation efficiency and fast in compared to the three de-emulsifiers.

The 50 µg/ml emulsifier was applied for different crude oils from the above mentioned oil fields with different w/o ratios (10 , 15 , 25) % . The higher concentration for all de-emulsifiers have better effect on reducing the surface tension and causes an easier penetration to the layer surrounding the water droplets. The Dgs has an excellent efficiency for all w/o ratios and for all de-emulsifer's percentages.

The study shows that Dgm has better separation efficiency in compared to Dom and nearly similar efficiency to the commercial de-emulsifier (Rp6000) for all (w/o) proportion and for all periods of times.

From this study we can conclude that the most important factors effecting the de_emulsification are temperature, type of oil, the concentration of the de-emulsifier and time⁽¹¹⁾ .

The prepared emulsifier, Dgm, can be used for the oil industry in Iraq, especially the technology of emulsification is restricted to the certain international companies, Southern oil company consumes about 50 barrel/day of Rp6000.

Aknoledgment:

We would like to express our thanks to Mr . Dawood Salim Abd for his assistance during this work .

References:

1. S. Ross and I. D. Morrison" *Colloidal systems and interfaces*", John wiley and sons, 132 , 267 , (1988).
2. Alfred Martin, *Physical Pharmacy*, John Wiley and Sons, London, 4th Ed,(1989).
3. F. M. Menger, C. A. Littau, *J. Am. Chem. Soc.*,113, 1451(2000).
4. D. Hummel "*Identification and analysis of surface active agents*" John Willy and sons, London(1968).
5. D. J. Shaw"*Introduction to colliod and surface chemistry*" Butter Worth , London , 2nd ed , 206 . (1970) .
6. Y. P. Zhu, A. Masuyama, Y . Kirito , M . okahata, *J . Am . oil chem. Soc.* 68 , 539(1991) .
7. Q. Rist, A. Rike, L.jones and H. J. Carison, *J. MacroMolecules* . 6 , 979 (2001).
8. R. S. Shelton, *J. Am. Chem. Soc*, 68, 1,753(1946).
9. "**Markiting specification of Iraqi petroleum products**" 217, Baghdad (1991).
10. T. Leslie, Ph. D. Thesis, Emory Univ. USA(1994).
11. Z. K. Kreamid, M. Sc. Thesis, Basrah university, Iraq(2004).

تحضير بعض منشطات السطوح التوأمية وتطبيقاتها في الصناعات النفطية

زيدون خلف كريم
وزارة النفط – شركة توزيع المنتجات النفطية

د. نزار عبد الامير حسين
جامعة البصرة – كلية التربية
العراق - البصرة

د. كوركيس عبد آل آدم
جامعة سدني
استراليا

ملخص البحث

منشطات السطوح التوأمية هي املاح رباعيه الامونيوم حضرت من ثلاثي مثيل الاثلين الثنائيه الامين مع سيتيل البروميدي بينما منشطات السطوح الاعتياديه والتي هي املاح رباعيه الامونيوم والتي حضرت من ثلاثي مثيل الامين مع سيتيل البروميدي شخصت بطرق التحليل العنصري وطيف الاشعه تحت الحمراء.

مقارنه كواسر الاستحلاب المحضره من منشطات السطوح الاعتياديه والتوأمية مع كواسر الاستحلاب التجاريه (Rp6000) اظهرت ان كواسر الاستحلاب التوأمية تمتلك خواص جيده نسبه الى كواسر الاستحلاب الاخرى.

لاستخدام منشطات السطوح الاعتياديه والتوأمية ككواسر استحلاب فقد اعتمدت مكونات كواسر الاستحلاب التجاريه حيث تم تحليل النتائج عن طريق التحليل العنصري و طيف الاشعه تحت الحمراء ودرجه الانصهار والذوبانيه ودرجه التالف وتحليل المجاميع الفعاله.

ان كفائه كواسر الاستحلاب المحضره قد فحصت بالطرق القياسيه وباستخدام مصادر نفطيه خام(حقول الفكه الشماليه والجنوبيه العراقيه) مع كفاءة كواسر الاستحلاب التجاريه (Rp6000).