



## THEORETICAL AND PRACTICAL STUDY OF SOME SURFACTANTS AND USE IN TREATMENT OF WATER IN CRUDE OIL (W/O) EMULSIONS

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### Abstract

Four types of surfactants derivatives of phthalic anhydride and alkyl amines consist of different length of hydrocarbon chains were prepared. The prepared surfactants were characterized by Infrared spectrophotometer and CHN analysis. The physical properties of the prepared de-emulsifiers were measured i.e. (pH, density, viscosity, CMC, molar conductivity and flash point). The efficiency of the prepared de-emulsifiers were studied with time and long side chain substituted. The hydrophilic-lipophilic balance (HLB) was calculated. The polarizability and dipole moment were studied by PM3 quantum mechanical method using the Hyperchem series program. The theoretical results were compared with the practical results.

### دراسة نظرية وعملية لبعض منشطات السطوح واستخدامها في معالجة مستحلبات الماء في النفط الخام (W/O)

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### الخلاصة

حضرت أربعة أنواع جديدة من منشطات السطوح المشتقة من تفاعل الفثاليك انهيدريد مع الكايل أمين حاو على سلسلة هيدروكاربونية معوضة بذرات كاربون مختلفة. شخضت منشطات السطوح المحضرة بتقنيتين أساسيتين هما مطيافية الأشعة تحت الحمراء وتحليل العناصر الدقيق. درست الخصائص الفيزيائية لكواسر الاستحلاب المحضرة والمتمثلة بـ (الدالة الحامضية، الكثافة، اللزوجة، الشد السطحي، التوصيل المولاري، التركيز الغروي الحرج و درجة الوميض). كما درست كفاءة الفصل وتأثير طول السلسلة على قابلية فصل الماء عن النفط. وتم حساب نظام الموازنة بين المجاميع المحبة للماء والمحبة للدهون. إذ اتقنت الدراسة العملية مع الدراسة النظرية وذلك من خلال رسم الشكل الهندسي للمادة المنشطة للسطح وحساب عزم ثنائي القطب بأن زيادة طول السلسلة الهيدروكاربونية المعوضة يؤدي إلى زيادة القطبية بسبب انتشار الشحنة على طول المركب مما يزيد من عملية الإذابة وتقليل الشد السطحي وسهولة فصل الماء عن النفط وتكوين مستحلب أكثر استقراراً.

### Introduction

Surfactants are important industrial commodity. Surfactants are usually classified in either of two general categories. Those are based on natural sources, the fatty carboxylic acid

salts and soaps. Historically, the soaps are first type of surfactants discovered, manufactured and used by humans[1]. The second type of surfactants is detergents. These are made form industrial organic

chemicals, usually petrochemicals. They have been "designed" by chemists for specific end-uses, and having certain desirable physical and chemical properties [2]. Surfactants are widely used in industrial processes for their favorable physicochemical characteristics such as detergency, foaming, emulsification, dispersion and solubilization effects. Such extensive applications of surfactants have produced environmental pollution and have raised problems in wastewater treatment plants. The experimental data have shown that surfactants can kill microorganisms at very low concentrations (1-5mg/L) and harm them at even lower concentrations (0.5mg/L). In addition, surfactants can produce foams, which are a significant problem in sewage treatment. Therefore, the removal of the surfactants from wastewater is important in reducing their environmental impact [3]. Many techniques have been used for removal of surfactants in aqueous solution. Among these, biological, degradation, ozonation and extraction are often costly and may possibly create secondary pollution because of excessive use of chemicals. In addition; a large number of surfactants used at present, like linear alkyl benzene sulphonates and have relatively low biodegradability[4]. The adsorption process seems to be an effective method for the removal of surfactants, especially in the case of low concentrations of surfactant. A number of adsorption systems have been explored for the removal of surfactants. Numerous adsorbents, such as silica, mineral oxides and natural biomasses, have been extensively investigated [4,5]

Surfactants are lowered the surface tension in the pesticide formulation or added to spray mixture, the pesticide-containing water droplets spread across the leaf surface instead of bending up, in addition to, the role surfactants is to decrease the surface tension of water by overcoming the barriers of solvent-solvent interactions[5]. In recent decades, four new surfactants is prepared from condensations of phthalic anhydride with fatty amines containing different chains ( $C_4$ ,  $C_8$ ,  $C_{12}$  and  $C_{16}$ ) and study

the physical properties such as (pH, CMC, Surface tension, Density, Viscosity, Flash point and Molar conductance), in addition it was used in (w/o) emulsions to know the effect of long chain on decreasing of surface tension and increasing the activity to separation of water from oil and comparing the practical results with theoretical one through chain length, polarizability and geometry shape by using the quantum chemical.

### Experimental:

#### A- Chemicals:

Phthalic anhydride, butyl amine, octyl amine, dodecyl amine and hexadecyl amine (Aldrich), sodium bicarbonate (BDH), xylene (BDH), urea (Aldrich) and sulphonic acid (Baji-Iraq).

#### B- Instruments:

1. Infrared spectrophotometer (U-1500) made by (HITACHI) in the range (4000-500)  $\text{cm}^{-1}$ , Department of Chemistry-College of Education-Basrah University.
2. Elemental analysis (CHN) model, Science College-Tehran University.
3. Electrical conductivity meter (JENWQY), made in (UK) which is consist of (voltmeter, sample cell and power supply), Department of Chemistry- College of Education-Basrah University
4. pH-meter (WTW) Germany from College of Science Basrah University (combined electrodes).
5. Density meter (density bottle glass).
6. Viscosity meter (viscometer glass).
7. Surface tension meter kind Telescope.
8. Freezing point osmometer type (OSMOMAT 030) College of Science-Basra University.

#### Synthesis of Surfactants[6]:

1.48g (0.01mole) phthalic anhydride and 0.73g (0.01mole) N-butyl amine was melted together in round bottom flask. After the melting 0.42g (0.005mol) of sodium bicarbonate was added and heated for (15min). The product was filtered, washed with ethanol then recrystallized twice from ethanol and dried in vacuum at  $10^{\circ}\text{C}$  for 1h. The yield obtained was (91%). The structure of the product is shown in Scheme (1-1).

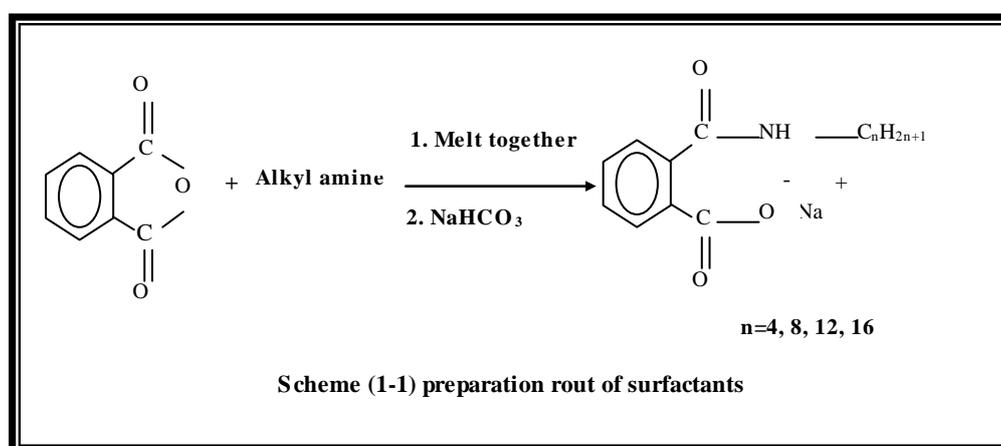
Similarly, the Sodium (N-octyl (2), dodecyl (3) and hexadecyl (4))-2-carboxyl benzamide were prepared as the above

procedure by (1:1) mole ratio but the difference in number of grams of alkyl amines as explained in Table (1). The

structures of the products are shown in Scheme (1-1).

**Table (1): molar ratio of alkyl amines with phthalic anhydride**

No.	Phthalic anhydride	Alkyl amines	Surfactants Name	Yield (%)
2	1.48g 0.01 mole	1.29g 0.01 mole	Sodium (N-octyl)-2-carboxyl benzamide	93
3	1.48g 0.01 mole	1.85g 0.01 mole	Sodium (N-dodecyl)-2-carboxyl benzamide	95
4	1.48g 0.01 mole	2.41g 0.01 mole	Sodium (N-hexadecyl)-2-carboxyl benzamide	96



### Synthesis of Surfactants Solutions De-emulsifiers:

8g (0.03mol) sodium N-(butyl, octyl, dodecyl and hexadecyl)-2-carboxyl benzamide, 6g (0.1mol) urea, 3g (0.01mol) sulphonic acid and 3g (0.01mol) oil were dissolved in 80ml xylene

[20:80] (W/V) to prepare the grade names of de-emulsifier agents MD<sub>1</sub>, MD<sub>2</sub>, MD<sub>3</sub> and MD<sub>4</sub> respectively, and used in treatment of (w/o) emulsions[6]. The physical properties of new surfactants solutions are listed in (Table 2).

**Table 2: values of physical properties of different prepared de-emulsifiers**

De-emulsifiers	pH	Density (g/cm <sup>3</sup> )	Viscosity (milipoice)	Surface Tension (dyne/cm)	Flash point (°C)	CMC (M)
MD <sub>1</sub>	6.6	1.6344	1.7113	185	40	3.2×10 <sup>-3</sup>
MD <sub>2</sub>	6.7	1.6671	1.7212	176	43	1.8×10 <sup>-3</sup>
MD <sub>3</sub>	6.8	1.6732	1.7268	170	47	3.6×10 <sup>-4</sup>
MD <sub>4</sub>	6.8	1.6765	1.302	166	51	1.9×10 <sup>-4</sup>

MD<sub>1</sub>, MD<sub>2</sub>, MD<sub>3</sub> and MD<sub>4</sub>= Grade name of de-emulsifiers

### Results and Discussion

#### Calculation of the Critical Micelle Concentration (CMC):

Critical micelle concentration (CMC) is the concentration which monomeric surfactant molecules abruptly aggregate to form micelles [7]. It is determined mostly by tensiometry,

conductometry, goniometry, etc. Using these techniques, CMC, shape and structure of micelle, surface activity, solubilization, adsorption, wetting, phase behaviour, etc. of surfactants can be accounted for.

The value of CMC decreases with increase in the hydrophobic chain length of the molecule.

Hydrophobic interaction opposed by electrostatic repulsion among the ionic head groups drives the process of micellization. The critical micelle concentration of the surfactant decreases due to lower surface tension of the oil droplets. At higher temperatures the effective surfactant concentration is greater than the CMC at lower temperature, thereby, decreasing the stability of the emulsion. A value of CMC data of surfactants determined by molar conductive method is presented in (Table 2) and (Figures 1, 2, 3 and 4).

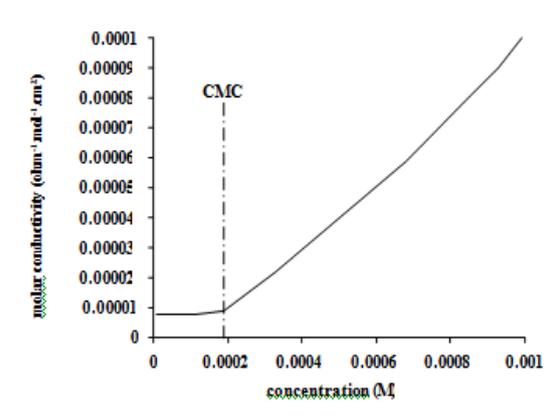


Figure 4: CMC calculated of MD<sub>4</sub>

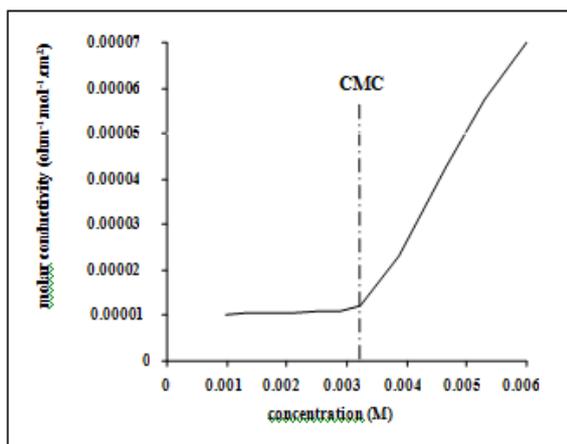


Figure (1) CMC calculated of MD<sub>1</sub>

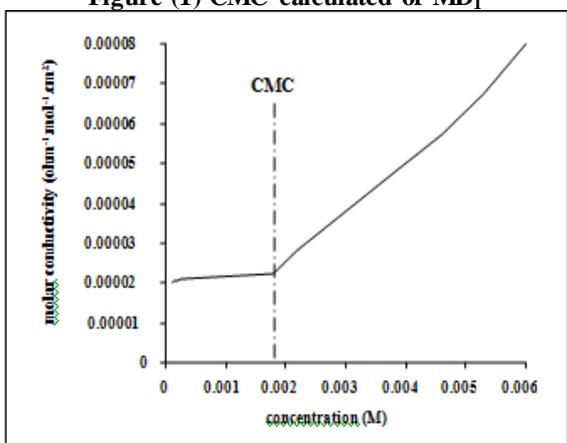


Figure 2: CMC calculated of MD<sub>2</sub>

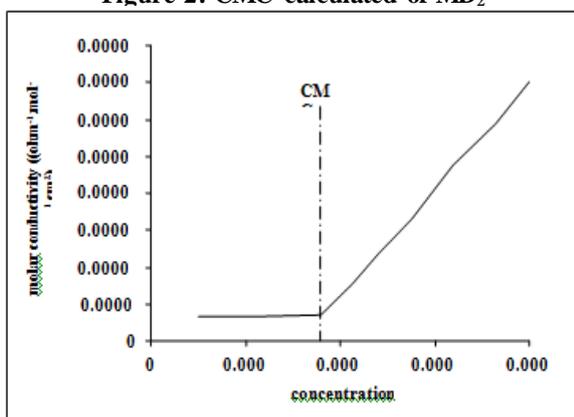


Figure 3: CMC calculated of MD<sub>3</sub>

**Selection of Surfactants:**

The selection of surfactants depends on hydrophilic-lipophilic balance (HLB) which was calculated by equation (1) [7]. The prepared surfactants were used water in oil emulsion (w/o) as shown in Table (3). This value then is an induction of the oil or water solubility of the product. The lower (HLB) number is more water- soluble the product; and in turn the higher (HLB) number is more oil- soluble the product [7].

$$HLB = 20 \times \frac{\text{mole wt. EO}^* \times \text{moles wt. EO}}{\text{mole wt. of adduct}} \dots (1)$$

- EO\* : The weigh of lipophilic-chain.
- EO : The weigh of hydrophilic-chain.
- Wt. of adduct: The weigh of surfactant.

Table 3: the application of surfactants

Value of HLB	Application
0-3	Anti-foaming
4-6	(w/o) emulsifying
7-9	Wetting
8-18	(o/w) emulsifying
13-15	Detergent
10-18	Solubilizing

**Separation Efficiency for Preparation of De-emulsifiers (Standard):**

The separation efficiency of de-emulsifiers is measured by taking samples of wet crude oil (water ratio 8%) and adding the de-emulsifiers with different concentrations at (30-50ppm) through supporting the separation with suitable factors representing with water bath at 60<sup>0</sup>C and shaking for 5min. Then the samples were heated in a water bath and the volume of separated water from the oil was recorded every 5min. The total time of separation is 30min. The volume of

separated water is tabulated in Tables (4, 5, 6 and 7).

**Table 4: the volume of water separated for MD<sub>1</sub>**

Concentration (ppm)	Average volume of separated water (ml)	Efficiency %
30	2.5	31.25
40	3.5	43.75
50	4.5	56.25

**Table 5: the volume of water separated for MD<sub>2</sub>**

Concentration (ppm)	Average volume of separated water (ml)	Efficiency %
30	3.3	41.25
40	4.5	56.25
50	5.6	70

**Table 6: the volume of water separated for MD<sub>3</sub>**

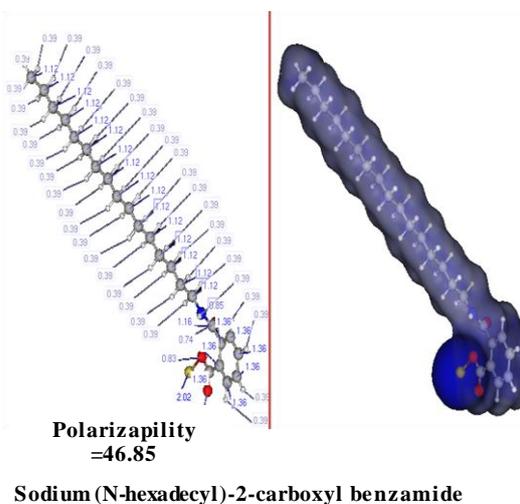
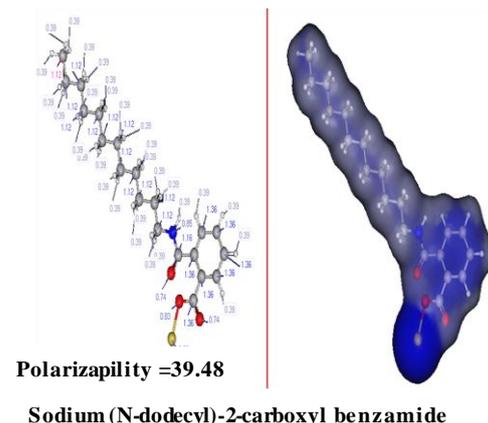
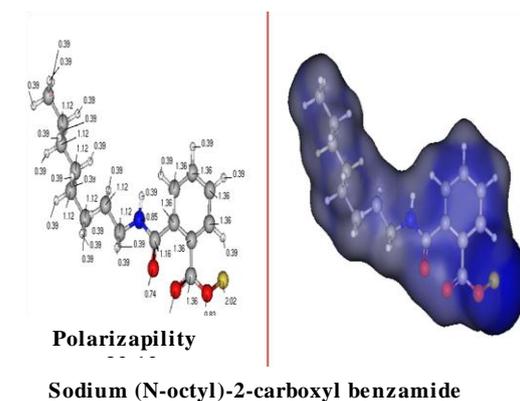
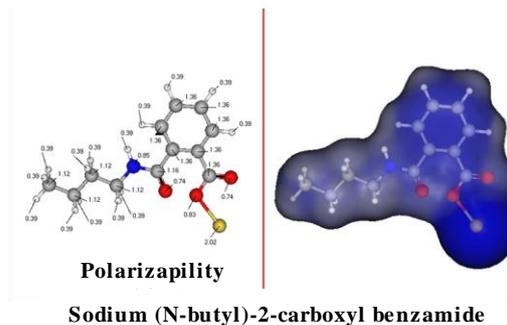
Concentration (ppm)	Average volume of separated water (ml)	Efficiency %
30	4.1	51.25
40	5.3	66.25
50	6.2	77.5

**Table 7: the volume of water separated for MD<sub>4</sub>**

Concentration (ppm)	Average volume of separated water (ml)	Efficiency %
30	5.7	71.25
40	6.5	81.25
50	7.5	93.75

### Computational Details:

Molecular geometries of all formed compounds were optimized using molecular mechanics and the semi-empirical PM3 quantum mechanical method using the Hyperchem series program [8]. Molecular mechanics technique was used to rapidly investigate the geometries of suggested structures. The size of these molecules considered in this paper, however, precludes a treatment by reasonably high level *ab initio* methods. Therefore, we have used semi-empirical (PM3) [9]. Molecular orbital calculations are a widely used semi-empirical molecular mechanics program. Given the dipole moment of all compounds as shown in Scheme (1-2).



**Scheme (1-2) the molecular geometries for surfactants [9]**

The phthalic anhydride was allowed to react with alkyl amine to yield surfactants of sodium (N-butyl, octyl, dodecyl and hexadecyl) -2-carboxyl benzamide [91%, 93%, 95% and 96%] respectively.

The surfactants appeared essential bands which may be returned to the stretching frequencies of (N-H) group at  $3330-3250\text{cm}^{-1}$ , (C=O) group at

$1665-1660\text{cm}^{-1}$ , (C-N) group at  $3180-3174\text{cm}^{-1}$  [10], (C-H) aromatic at  $3090-3080\text{cm}^{-1}$ , (C-H) aliphatic at  $2920-2850\text{cm}^{-1}$  and  $725-720\text{cm}^{-1}$ , (C-O) at  $1265-1260\text{cm}^{-1}$ , (C-C) at  $910-893\text{cm}^{-1}$  and (C=C) at  $1580-1570\text{cm}^{-1}$  [10].

**Table 8: The absorption frequencies of some important bands**

Surfactants	Wave numbers( $\text{cm}^{-1}$ )						
	$\nu(\text{C-H})$	$\nu(\text{C-C})$	$\nu(\text{C-N})$	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C-O})$	$\nu(\text{C=C})$
Sodium (N-butyl)-2-carboxyl benzamide	al.2890 ar.3030, b.725	893	3175	3250	1660	1260	1580
Sodium (N-octyl)-2-carboxyl benzamide	al.2895 ar.3032, b.730	899	3178	3265	1662	1262	1575
Sodium (N-dodecyl)-2-carboxyl benzamide	al.2918 ar.3033, b.735	907	3180	3300	1665	1264	1570
Sodium (N-hexadecyl)-2-carboxyl benzamide	al.2920, ar.3030, b.735	910	3180	3330	1665	1265	1580

al-aliphatic, ar-aromatic, b- bending and long chain

Elemental analysis (C, H, N) shows the practical and theoretical values in (Table .9)

**Table 9: Elemental analysis of the products**

Surfactants	Practical Value %			Theoretical Value %		
	C	H	N	C	H	N
Sodium (N-butyl)-2-carboxyl benzamide	59.18	5.59	5.73	59.25	5.76	5.76
Sodium (N-octyl)-2-carboxyl benzamide	63.95	6.91	4.53	64.21	7.35	4.68
Sodium (N-dodecyl)-2-carboxyl benzamide	67.14	7.88	3.82	67.60	8.45	3.94
Sodium (N-hexadecyl)-2-carboxyl benzamide	69.89	8.91	3.22	70.07	9.24	3.40

The (HLB) values are calculated to the prepared surfactants by equation (1), and the results are explained in (Table 10).

**Table 10: the value of HLB**

Surfactants	Value of HLB
Sodium (N-butyl)-2-carboxyl benzamide	4.9
Sodium (N-octyl)-2-carboxyl benzamide	5.3
Sodium (N-dodecyl)-2-carboxyl benzamide	5.6
Sodium (N-hexadecyl)-2-carboxyl benzamide	5.9

The separation efficiency was measured to the de-emulsifiers. It is noticed that the efficiency increases with increasing the length of substituted chain due to the chain solubility in crud oil and breaking emulsion so this leads to increase the volume of separated water as explained in Tables (4, 5, 6 and 7). These results are as same as the theoretical results through increasing the polarizability which is produced from the distribution of charge around the surfactants that consist of long substituted chain; this is shown clearly in Figures (5 and 6).

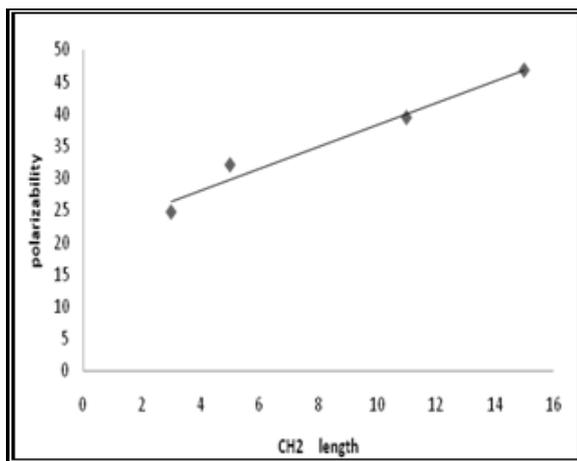


Figure 5: the relation between polarizability and length chain

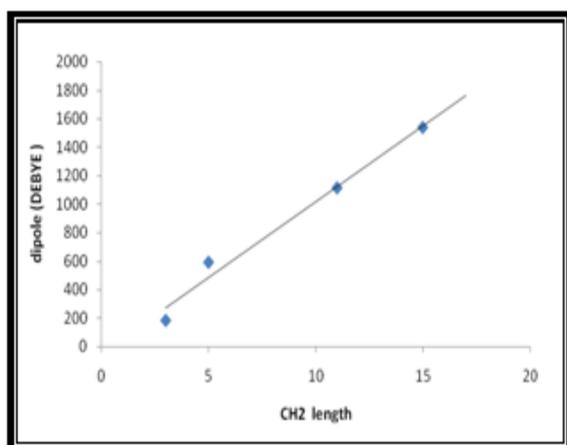


Figure 6: the relation between dipole and length chain

The physical properties of de-emulsifiers are measured as shown in Table (2). The Critical Micelle Concentration (CMC) for de-emulsifiers are calculated from the relation between the molar conductivity and the concentration as explained in Figures (1, 2, 3 and 4). The value of CMC decreases with increase in the hydrophobic chain length of the molecule due to hydrophobic interaction opposed by electrostatic repulsion among the ionic head groups drives the process of micellization, in addition to the critical micelle concentration of the surfactant decreases with shortage surface tension of the oil droplets as shown in Table (2).

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