Synthesis, Characterization and Evaluation of dipotassium dodecyl diphenyl ether disulfonate as anionic surfactant inside in synthesis the Emulsion polymer Lattices

Yonis Ahmed Ismael[*], Asaad Faisal Khattab[**] and Ahmed Taher El-Habab[***]
[*] Department of Chemical Science, Collage of Science, University of Mosul, Mousl, Iraq
[**] Department of Chemical Science, Collage of Science, University of Mosul, Mousl, Iraq
[***] Department of chemical Science, Collage of Science, Zagazig University, Zagazig, Egypt
E-mail: [*]Younis_kim@yahoo.com, [**] asaadfaisal@uomosul.edu.iq, [***]chemist.ahmed.taher@gmail.com

ABSTRACT

The presence of anionic surfactant in mixture with a non-ionic surfactant usually results in an increase in the cloud point of the non-ionic component. Indicating that the ionic component is forming mixed micelles with the non-ionic surfactant. In this study the anionic surfactant is dipotassium dodecyl diphenyl ether disulfonate designated as (DPDDPEDS), was synthesized. The structure was characterized by using spectroscopic measurements. In addition, its surface properties and foaming properties were investigated. The results indicated that DPDDPEDS exhibits excellent surface activity. It was found that the DPDDPEDS as anionic surfactant have low krafft point approximation 10 ºC.

Keywords: DPDDPEDS. LME-EO-30. Surfethoxymer.

تحضير وتوصيف وتقييم ثنائي بوتاسيوم دوديسيل ثنائي فينيل إيثر ديسلفونات كمادة خافضة للتوتر السطحي الأنيونية داخل في تركيب شبكات البوليمر المستحلب

يونس أحمد إسماعيل*، أسعد فيصل خطاب**، أحمد طاهر الحباب***
* قسم الكيمياء، كلية العلوم، جامعة الموصل، الموصل، العراق
** قسم الكيمياء ، كلية العلوم، جامعة الموصل، الموصل، العراق
***قسم الكيمياء ، كلية العلوم، جامعة الزقازيق، الزقازيق، مصر

الخلاصة

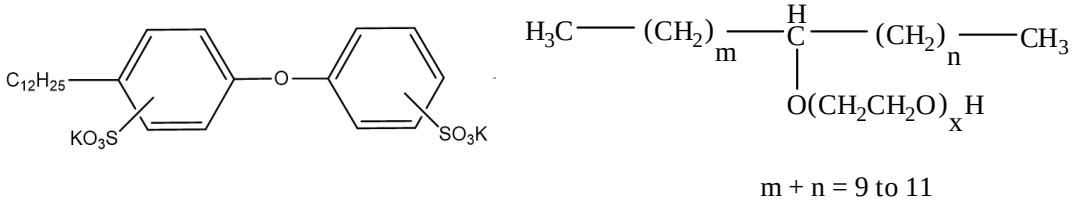
عادةً ما يؤدي وجود مادة خافضة للتوتر السطحي أنيونية في خليط مع مادة خافضة للتوتر السطحي غير أيونية إلى زيادة نقطة السحابة للمكون غير الأيوني. مما يشير إلى أن المكون الأيوني يشكل مذيلات مختلطة مع المادة الخافضة للتوتر السطحي غير الأيونية. في هذه الدراسة تم تصنيع المادة الفعالة السطحي الأنيونية وهي ثنائي بوتاسيوم دوديسيل ثنائي فينيل إيثر ثنائي سلفونات والمسمى بـ (DPDDPEDS). وتم تشخيص التركيب باستخدام القياسات الطيفية. بالإضافة إلى ذلك، تم دراسة خصائصه السطحية وخصائص الرغوة. أشارت النتائج إلى أن DPDDPEDS يُظهر نشاطًا سطحيًا ممتازًا. وقد وجد أن DPDDPEDS كمادة خافضة للتوتر السطحي أنيونية لها نقطة كرافت عند 10 درجة مئوية.

الكلمات المفتاحية: ثنائي بوتاسيوم دوديسيل ثنائي فينيل إيثر ثنائي سلفونات، لؤريل ميرستايل الكحول اثيوكسيل 30 و سيرفي ثوكسيمر.

1. INTRODUCTION

The characteristic structural feature of surface-active agents is a molecular structure containing a group which has a strong attraction for the solvent (called the lyophilic group) together with a group which has very little attraction for the solvent (the lyophobic group). When used in water the terms are hydrophilic and hydrophobic, respectively. The hydrophobic group is usually a long chain hydrocarbon residue, occasionally an halogenated or oxygenated hydrocarbon residue; the hydrophilic group is an ionic or highly polar group. Molecules containing both Iyophilic and lyophobic groupings are called amphipathic molecules; a surfactant [1,2]. The negative charge of the hydrophilic portion is the main property of the anionic surfactant class. Due to their availability and low cost, anionic surfactants are generally known as the most widely used surfactants in the petroleum industry. Anionic hydrophilic groups commonly consist of sulfate, sulfonate, carboxylate, and phosphate groups [3].Surfactant act to decrease interfacial tension between monomer and aqueous phase, stabilize the latex and generate micelles in which monomers emulsified and nucleation reaction proceed. Surfactants increase particle number and decrease particle size, these surfactants may be anionic surfactants such as fatty acid soaps (sodium or potassium stearate, laurate, palmitate), sulfates, sulfonates (sodium lauryl sulfate and sodium dodecyl benzene, as well as the surfactants are key additives in water-borne coatings for emulasions, The main components of emulsion polymerization media involve monomer(s), dispersing medium, emulsifier, and water-soluble initiator [4-7]. The dispersion medium is water in which hydrophobic monomers is emulsified by surface-active agents (surfactant). When surfactant concentration exceeds critical micelle concentration (CMC) it aggregate in the form of spherical micelles, so surface tension at the surface decrease, as a result hydrophobic monomers enter in to the vicinity of micelle and reaction continue until all monomer droplets are exhausted and micelle containing monomers increase in size.In this work, dipotassium dodecyl diphenyl ether disulfonate (DPDDPEDS) is prepared. DPDDPEDS is a highly efficient and multifunctional anionic surfactant with two hydrophilic head groups. The structure of DPDDPEDS can be seen in Scheme 1a. It has unique double sulfonate hydrophilic groups, which are linked by a rigid diphenyl ether group which produces intramolecular hyperconjugation. DPDDPEDS has a variety of advantages when compared with traditional non-ionic surfactants as LMAEO-30 surfactant is represented in Scheme 1b excellent water solubility, coupling properties [8-10], extremely low Krafft point, excellent dispersion capacity [11-13], good hard water, bleach tolerance [14], and good stability in strong acid, strong alkali, and concentrated electrolyte solution [8,15]. Conventional surfactants are small and mobile and these surface-active molecules can migrate to the surface layer of a polymeric film. This kind of action can have a negative effect on the application properties

e.g. adhesion and water resistance of pressure-sensitive adhesives. One approach to alleviate the surfactant migration problem is to adopt a polymerizable surfactant, which has a carbon-carbon double bond and can be chemically incorporated into the latex particles during polymerization [16].



a **b**

Scheme 1: The structure of (a) DPDDPEDS-surfactant. (b) LMAEO-30-surfactant

2. MATERIAL AND METHOD

2.1 Materials

The reagents used in this experimental study include Dodecyl alcohol (Aldrich), Diphenyl ether (Aldrich), Potassium hydroxide (KOH, 99%), fuming sulfuric acid H_2SO_4, Hydrochloric acid HCl, Methylene chloride (CH_2Cl_2), OP-EO-9 (trade name TRITON^{TM} X-100 surfactant).

2.2. Synthesis of DPDDPEDS anionic surfactant

DPDDPEDS was synthesized by using diphenyl ether, dodecyl alcohol and fuming sulfuric acid as main starting materials.

The first step comprising preparing dodecyldiphenyl ether by reacting the dodecyl alcohol with diphenyl ether in the presence of H_2SO_4 to obtain a mixture of monododecyl diphenyl ether and didodecyl diphenyl ether. The number of alkyl substituents per diphenyl ether molecule can be controlled by adjusting the relative proportions of the reactants.

The second step in which the mixture of monododecyl diphenyl ether and didodecyl diphenyl ether is subsequently reacted with fuming sulfuric acid as a sulfonating agent in a methylene chloride as an inert solvent.

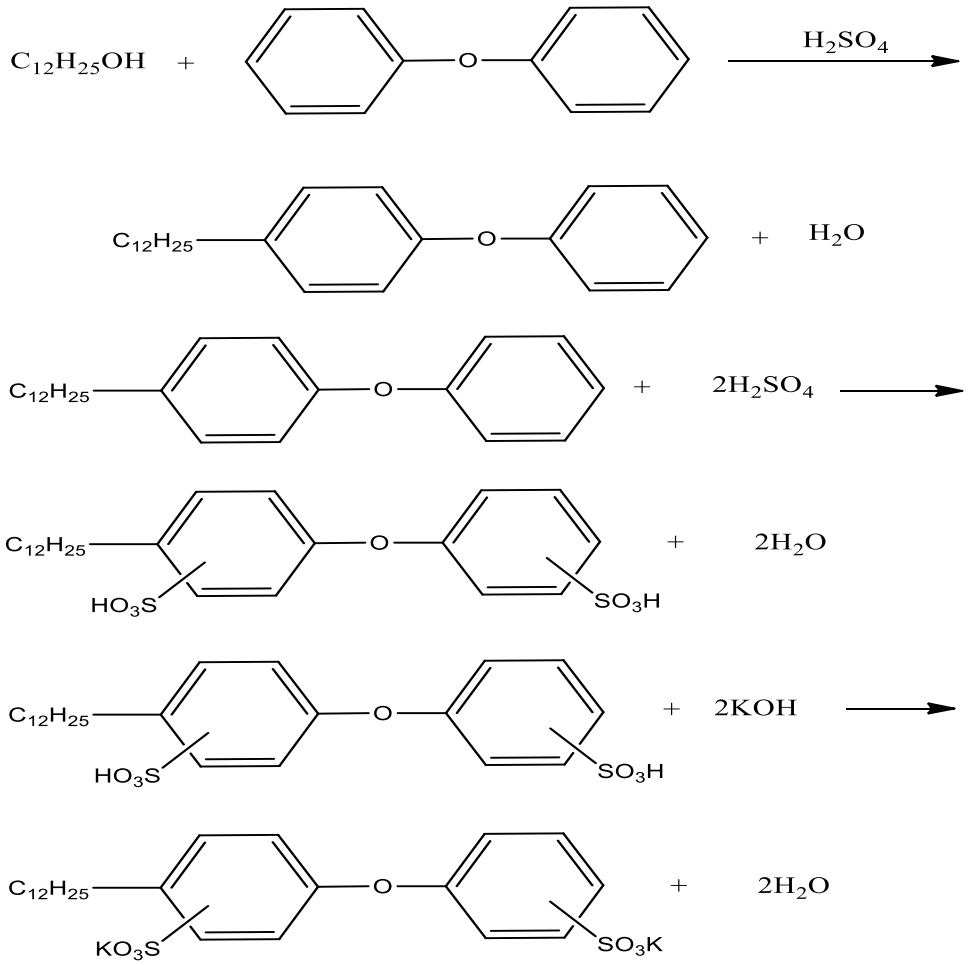
The third step comprising neutralization of the diluted acid with an alkaline base such as Potassium hydroxide.

Finally, the crude product was dissolved in hot ethanol, the hot filtration to remove the inorganic salt, and recrystallized several times.

The final product yield is 42.0 %. Scheme 2 show the mechanism of the preparation of DPDDPEDS as anionic surfactant.

2.3 Effects of reaction variables on Synthesis of (DPDDPEDS)

Study of the effect of different molar ratio of dodecyl alcohol to diphenyl ether, reaction temperature, reaction time and different molar ratio of dodecyl diphenyl ether to fuming sulfuric acid on yield are investigated.



Scheme 2: Mechanism of the preparation of DPDDPEDS as anionic surfactant

2.4 Characterization of the prepared DPDDPEDS

2.4.1 Instrumental Analysis

The chemical structure of DPDDPEDS was confirmed by the FTIR and ^{1}H-NMR. FTIR was carried out using Pye Unicam SP1200 spectrophotometer using KBr Wafer technique in the region from 4000 to 500 Cm^{-1}. 1 H-NMR spectra were determined on Varian Gemini 200 MHZ (CDCl3) using TMS as internal standard (chemical shift in d-scale).

2.4.2 Surface Tension Measurements

The surface tension measurements were carried out for different concentrations of the prepared anionic surfactant dissolved in bi distilled water with a Du NouyTensiometer (Kruss Type 6) (Krüss GmbH, Hamburg). The Tensiometer was calibrated using method described in Designation in [ASTM D1331-89,2001] [17] with a Krüss Tensiometer operates on the Du Nouy principle, in which a platinum-iridium ring is suspended from a torsion balance, and the force (in mN/m) necessary to pull the ring free from the surface film is measured at

constant temperature (25±1ºC) [18]. The solutions were left for 2 hours to allow the stabilization and complete adsorption at the solution surface then apparent surface tension values were given as a mean of three replicates.

2.4.3 Critical Micelle Concentration (CMC)

The critical micelle concentration (CMC) and the surface tension at the critical micelle concentration (CMC) are important parameters to assess the surface activity of surfactants [19]. Surface tension measurements were used to calculate the critical micelle concentrations (CMCs) of the prepared compound. In this method, the surface tension values of prepared surfactant aqueous solutions were plotted against the corresponding concentrations. The critical micelle concentrations are expressed by the interrupt change in the surface tension-concentrations curves.

2.4.4 Hydrophilic – Lipophilic Balance (HLB)

Griffin's hydrophilic-lipophilic balance (HLB number) is a semi-empirical scale for choosing surfactants [20]. The relative proportion of hydrophilic to lipophilic (hydrophobic) groups in the surfactant molecule serves as the basis for this scale (s). The hydrophilicity of a surfactant is represented by the HLB number (0–20), which rises as hydrophilicity increases. The elevated CMC with HLB is a common general trend in a family of surfactants. HLB values were calculated as follows with the Griffin formula based on the ethylene oxide moiety in the molecule [21] as follows:

$$HLB = \frac{\%\ wt\ of\ ethylene\ oxide\ in\ the\ molecule}{5}$$

$$HLB = 20 \times \frac{MWH}{MWH\ + MWL}$$

Where,

MWH = Mol. Wt. of hydrophilic part.

MWL = Mol. Wt. of lipophilic part

2.4.5 Krafft point of the prepared anionic surfactants

The Krafft point was determined by keeping track of the temperature at which 1% weight/weight surfactant solutions become transparent during steady heating or first form precipitate upon cooling. The Kraft temperature was defined as the solution temperature at which the final crystal is rendered invisible by a light-intensity laser beam [22]. Solutions were first left to cool at -20^{o}C in the freezer overnight to ensure complete precipitation of the compounds in the form of hydrated crystals. The solutions were gently shaken every 10 minutes and the presence or absence of precipitate noted. The temperature was tuned 0.5 ^{o}C by 0.5 ^{o}C from 10.0^{o}C to at least 5 ^{o}C above the Krafft temperature. Krafft temperature is the same as that required to completely dissolve the hydrated

solid surfactant, judged visually to be the point of complete clarification of the solution.

2.4.6 Measurements of foaming properties

According to [ASTM D1173-07 (2007)] [23] In our experiments [24], a certain amount of the prepared non-ionic surfactant and surfethoxymers (typically 0.1wt% of aqueous surfactant solution) was pre-emulsified by stirring for 10 min on a magnetic stirrer. The obtained emulsion was additionally homogenized by several hand shakes before placing it into the glass cylinder of the Ross-Miles test (volume 1 L, internal diameter 37 mm) as shown in Fig. 1.

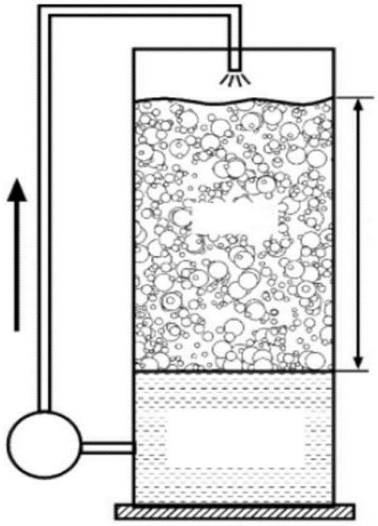


Fig. 1: Schematic presentation of Ross-Miles test.

The solution was circulated for 20 s, with a flux of 125 mL/s, through an orifice (7 mm diameter), which was placed at 23 cm above the level of the liquid. The initial foam volume (after stopping the circulation) is a measure of solution foaminess. The further change of the foam volume with time, $V_F(t)$, characterizes the foam stability. During the circulation of the liquid, dynamic foam was formed which had almost constant height/volume after, *e.g.*, 30 seconds of circulation. The steady-state height of the dynamic foam was measured and called hereafter the Dynamic Foam Height (DFH) – this height was used as a quantitative measure for the foamability of the solutions.
Foam stability was calculated by using the following formula [25]

$$Foam\ stability\ (\%) = \frac{Foam\ volume\ after\ 5\ minutes}{Foam\ volume\ after\ 0\ minutes} \times 100$$

3. RESULTS AND DISCUSSION

3.1 Effects of reaction variables on Synthesis of DPDDPEDS anionic surfactant

3.1.1 Effect of different molar ratio of dodecyl alcohol to diphenyl ether on yield of dodecyl diphenyl ether

Dodecyl alcohol and diphenyl ether molar ratio affect the yield. Fixed reaction time was 6 h, the reaction temperature is 70 ◦C. The molar ratio of the reactants impact on the yield, the results are shown in Table 1.

Table 1: Influence of dodecyl alcohol and diphenyl ether molar ratio on yield.

	n (Dodecyl alcohol): n (Diphenyl ether)				
	1:1	1:1.25	1:1.5	1:1.75	1:2
Yield %	86	91	97.5	97.5	96.9

Selecting the dodecyl alcohol and diphenyl ether molar ratio of 1.00:1.50 is more appropriate, while continuing to increase the amount of diphenyl ether to 2, the rate not changed and is not economical for the industrial production.

3.1.2 Effect of reaction temperature on the yield of dodecyl diphenyl ether

Study of the reaction temperature on the yield of dodecyl diphenyl ether is carried out which fixed reaction time was 6 h and Dodecyl alcohol and diphenyl ether molar ratio was 1.00:1.50. The reaction temperature impact on the yield, the results are shown in Table 2.

Table 2: Effect of reaction temperature on yield

	t / ^{o} C			
	45	**60**	**70**	**85**
Yield %	16.5	63.4	97.5	76.7

At about 70 ^{o}C reaction is more appropriate, at this temperature higher yield is achieved. While raised to 85 ^{o}C, the yield declines.

3.1.3 Effect of reaction time on the yield of dodecyl diphenyl ether

Study of the reaction time on the yield of dodecyl diphenyl ether is carried out which fixed reaction temperature was 70 ^{o}C and Dodecyl alcohol and diphenyl

ether molar ratio was 1.00:1.50. The reaction time impact on the yield, the results are shown in Table 3.

Table 3: Effect of reaction time on yield

	t / h			
	2	4	6	8
Yield %	38	87.5	97.5	97.9

Choice reaction time 6 h is more appropriate, while continuing to increase the reaction time, the rate not changed and is not economical for the industrial production.

3.1.4 Effect of different molar ratio of dodecyl diphenyl ether to fuming sulfuric acid on yield

Dodecyl diphenyl ether to fuming sulfuric acid molar ratio affect the yield. Fixed reaction time was 2 h, the reaction temperature is 35 ^{o}C. The molar ratio of the reactants impact on the yield, the results are shown in Table 4.

Table 4: Influence of Dodecyl diphenyl ether to fuming sulfuric acid molar ratio on yield

	n (Dodecyl diphenyl ether) : n (Fuming sulfuric acid)				
	1:1.8	1:2	1:2.4	1:2.6	1:2.8
Yield %	24	30.5	37.5	42	42.5

Selecting the Dodecyl diphenyl ether to fuming sulfuric acid molar ratio of 1.00: 2.6 is more appropriate, while continuing to increase the amount of fuming sulfuric acid to increase the yield, the rate not changed and is not economical for the industrial production.

3.2 Instrumental Analysis

According to the generalized structure for DPDDPEDS in Table 1a the structural moieties that can be spectroscopically justified by infrared spectroscopy for the DPDDPEDS anionic surfactant are summarized in Table 5, Fig.2 represents FTIR spectrogram of DSDDPEDS anionic surfactant.

Table 5: Assignment of the IR-absorption bands to the DSDDPEDS surfactant.

Structural moiety	Wave numbers in cm^{-1}	Assignment of the infrared absorption bands
Aromatic compounds (Benzene	3,070–3,010	ν (sp^2C–H)

ring)		1,570 w, 1,513 s, 1,486 w	ν (sp^2C=C), Aryl
para-substitution		831 s	ν (CH), Aryl (No ring bending)
		2,000–1,650	Pattern of overtones and combination Vibrations
CH_2-O for alcohols and ethers		≈ 1455 s	ν (sp^3C–H) Bending vibrations
For alkanes CH_3		$\nu_{as} \approx 2965$, $\nu_{s} \approx 2875$ and $I(\nu_{as}) > I(\nu_{s})$	ν (sp^3C–H) CH stretching vibrations, ν_{CH}< 3,000
For alkanes CH_2		$\nu_{as} \approx 2925$, $\nu_{s} \approx 2855$ and $I(\nu_{as}) > I(\nu_{s})$	ν (sp^3C–H) CH stretching vibrations, ν_{CH}< 3,000
		≈ 2,900 (weak intensity; mostly overlaid)	ν (sp^3C–H) CH stretching vibrations, ν_{CH}< 3,000
SO_3K	≈ 966 - 1,42(	ν_{s} (SO_3K) symmetrical stretching vibrations	
	≈ 935-1025	ν_{as} (SO_3K) asymmetrical stretching vibrations	
	622	δ_{s} (SO_3K) symmetrical Bending vibrations	
	470	δ_{as} (SO_3K) asymmetrical Bending vibrations	

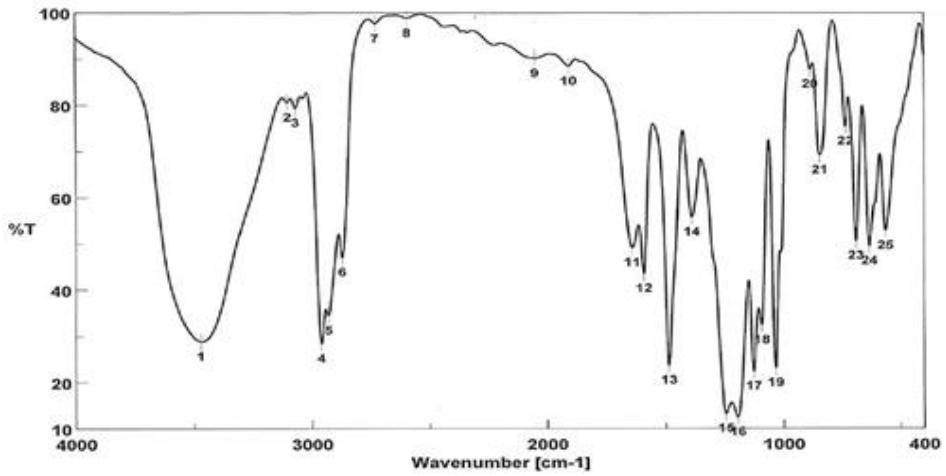


Fig. 2: FTIR spectrogram of the DPDDPEDS anionic surfactant

^{1}H-NMR spectrogram (300 MHz, $CDCl_3$) for the DPDDPEDS anionic surfactant in $CDCl_3$ is shown in Fig. 3 is: δ 7.77 (m, –*Ar*–), 7.54 (m, –*Ar*–), 7.28 (m, –*Ar*–), 7.02 (m, –*Ar*–), 6.80 (d, –*Ar*–), 3.28 (s, –Ar–C**H$_2$**–$(CH_2)_{10}CH_3$), 2.50 for DMSO Residual ^{1}H signal, 1.56 (m, –Ar–CH_2–C**H$_2$**–$(CH_2)_9CH_3$), 1.24 (m, –Ar–CH_2–CH_2–(C**H$_2$**)$_9CH_3$), 0.8 (m, –Ar–CH_2–CH_2–$(CH_2)_9$C**H$_3$**).

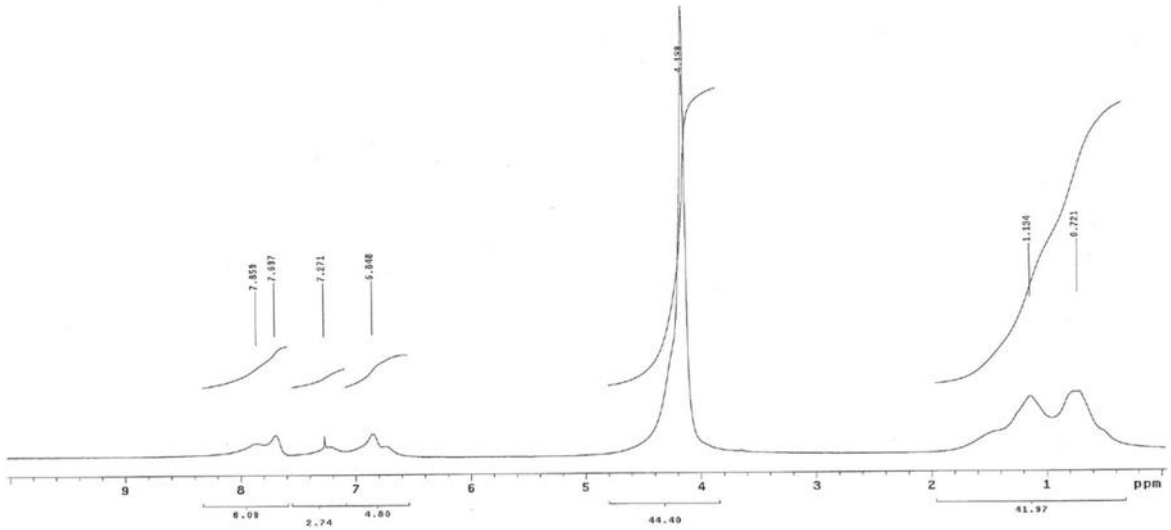


Fig. 3: ^{1}H NMR spectra of the DPDDPEDS anionic surfactant in DMSO-d6

3.3 Surface active properties of the DPDDPEDS

A variety of concentrations above and below the critical micelle concentration were used to measure the surface tension (γ) of the prepared anionic surfactant (C_{cmc}). For the anionic surfactant that was prepared in double distilled water, Fig. 4 shows plots of versus lnC concentration.

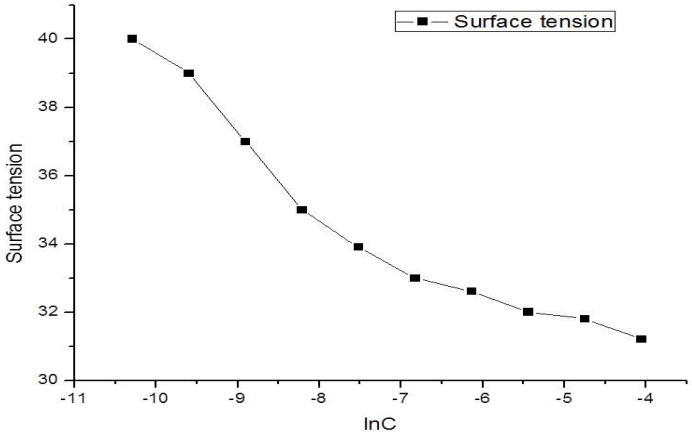


Fig. 4: Variations in surface tension with the DPDDPEDS concentrations in water at 25 °C.

A linear decrease in surface tension was seen as the surfactant concentration was increased, as shown by the surface tension curve, which has an obvious descending trend with increasing concentrations of surfactant in aqueous solution. This shows the high adsorption propensity of the surfactant molecules at the water-air interface. As a result, by boosting the concentration of surfactant molecules, the surface tension values remain almost constant. The concentration at which the surfactant micelles form is indicated by the intercept of these two regions (C_{cmc}) [26].

This observation was recorded for the prepared anionic surfactant up to the C_{cmc}, beyond which no considerable changes were noticed. The C_{cmc} data obtained from the break point in the γ- lnC plots are shown in Table 6 The critical micelle concentration (C_{cmc}) value of the synthesized anionic surfactant was extracted from the surface tension /concentration profiles.

Table 6: Surface tension (γ) and critical micelle concentration (C_{cmc}) of the DPDDPEDS at 25 °C

Surfactant code	γ_{cmc} (mN m^{-1})	C_{cmc} X 10^{-3} (mol dm^{-3})	HLB
DPDDPEDS	33.9	0.542535	18.658

3.4 Hydrophilic–Lipophilic Balance (HLB) of the DPDDPEDS

Table 6 shows HLB value calculated with the Davies and Rideal formula for the prepared DPDDPEDS anionic surfactants.

Based on the results, The HLB for the prepared surfactant made it suitable for oil in water industrial applications like emulsion polymerization.

3.5 Measurements of the Krafft point

In practice, the lower the Krafft Temperature, the more efficient the surfactant is in hot and cold-water applications. Table 7 gives the values of the Krafft temperature measured for the prepared DPDDPEDS anionic surfactant.

Table 7: The values of the Krafft temperatures measured for the DPDDPEDS

1% wt./wt.-solutions of surfactants	T_{Krafft} (^oC)
DPDDPEDS*	10
SLS	22

The value obtained in this work for SLS (Sodium lauryl sulfate) 22 ^oC is in good agreement with previous works [27,28]. It is well known that the Krafft Temperature is strongly dependent on the alkyl chain length, the type of polar head, particularly the nature of the counter-ion and head group interactions (including hydrogen bonding) [29]. When a polar segment is introduced between the alkyl chain and the ionic group of an ionic surfactant, the Krafft temperature is usually reduced [29], as it is observed in the case of DPDDPEDS surfactant, the Krafft temperature of which lower than SLS.

3.6 Measurements of foaming properties by Ross-Miles Foaming test

The foam height of the prepared DPDDPEDS anionic surfactant was measured and compared with the commercial non-ionic surfactants such as OP-EO-9 (Octyl Phenol ethoxylation 9 mole ,TRITON™ X-100 surfactant is trademark of the Dow chemical company) [30] and are shown in Table 8.

Table 8: Initial and five-minute Ross Miles foam heights for the prepared anionic and non-ionic surfactants

Surfactant 0.10 Wt.% solutions	Initial foam height, mm (DFH)	Foam height, mm after 5 min.	Foam stability (%)
DPDDPEDS	140	130	92.85
OP-EO-9	128	107	83.59

It can be seen that the prepared DPDDPEDS anionic surfactant has higher foaming heights than the prepared non-ionic surfactants. The foam stability for the prepared surfactants was ranked as; DPDDPEDS > OP-EO-9 (92.85, 83.59, respectively). All nonionic surfactants exhibited foam height and foam stability lower than the prepared DPDDPEDS anionic surfactant, this means that the ionic surfactants have highly charged surface film on their foams, leads to increase its height and stability. these results are in consistency with the data reported elsewhere [31]. It is clear that the highest foam was observed for the DPDDPEDS surfactant, due to possessing higher surface activities (extra low surface tension).

In previously published research since it was measured cloud point (C.P) for novel surface-active monomer (Surfethoxymers such as Hemi Ester Lauryl Myrisityl Alcohol Malite designated as HELMEM, HELMEI (Itaconate) and HELMES (Siccinate) as shown in the table 9, it was noticed cloud point is lower than the reactive temperature, it cannot be used independently and should compound with ionic surfactants. General reactive temperature of emulsion polymerization is at about 80 ℃. High temperature breaks the hydrogen bonds

and effects solution stability. It illustrates that the cloud point of HELMEM, HELMEI and HELMES is not suited alone for use in emulsion polymerization, as its cloud point is below the threshold of 80 ◦C [32]. The presence of an ionic surfactant in mixture with a nonionic usually results in an increase in the cloud point of the nonionic component. indicating that the ionic component is forming mixed micelles with the nonionic surfactant, thereby increasing its ‘‘solubility’’ at higher temperatures [33,34].

Many mixtures of surfactants, especially ionic with nonionic, exhibit surface properties significantly better than do those obtained with either component alone. Such synergistic effects greatly improve many technological applications in areas such as emulsion polymerization, surface tension reduction, cosmetics products, pharmaceuticals, and petroleum recovery [35].

The use of mixed surfactant systems should always be considered as a method for obtaining the optimal performance for any practical surfactant application.

Table 9: Cloud point values for prepared surfethoxymers.

Surfactant	Cloud Point, ^{o}C
HELMEM	68
HELMEI	56
HELMES	66

We measured the cloud point temperatures for binary mixtures of HELMEM surfethoxymers and DPDDPEDS anionic surfactant, as this combination of anionic and non-ionic surfactants represent those commonly and conjointly present in practical applications of surfactants.

Table 10: Effect of DPDDPEDS surfactant on cloud point of 1% solution of HELMEM surfethoxymer

% of DPDDPEDS in total surfactant	Measured CP, ^{o}C
0.20	75
0.30	83
0.40	87
0.50	89
0.75	92
1.0	96

The addition of very small amounts of DPDDPEDS surfactant to the solution of the prepared non-ionic HELMEM surfethoxymer drives cloud points higher. This is a very practical demonstration of the efficient coupling ability of the DPDDPEDS surfactant with other non-ionic surfactants. The results reveals that the increase of DPDDPEDS concentration led to increase the values of cloud point. This can be explained by the power of DPDDPEDS as an a micelles and increased spreading power in the medium.

Conclusion

The study aimed to Synthesis, Characterization, and Evaluation of DPDDPEDS as anionic surfactant and to develop novel lattices with good water repellency, weather resistance, and thermal stability for coating applications via preparing DPDDFEDS where the interaction between dodecyl alcohol with diphenyl ether in the presence of fuming surfuric acid produce dipotassium dodecyl diphenyl ether disulfunate designated as (DPDDFEDS) anionic surfactant has been synthesized successfully.

(DPDDFEDS) chemical structure was confirmed by I.R spectra and ^{1}H-NMR its surface active properties such as surface tension measurement, CMC, foaming properties by Ross-Miles and their Hydrophilic-lipophilic balance (HLB) have been investigated, the surface tension for (DPDDFEDS) anionic surfactant decreases with increasing concentrations of surfactant aqueous solutions. That indicates the high adsorption tendency of the surfactant molecules at the water interface.

krafft point of DPDDPEDS compared with SLS found that DPDDPEDS surfactant have low krafft point approximation 10 ºC, this means that more efficient the surfactant is in hot and cold-water applications.If cloud point for non-ionic surfactant is lower than the reactive temperature of emulsion polymerization which was 80 ^{o}C, it cannot be used independently this applies to surfethoxymers, and should compound with ionic surfactants This is a very practical demonstration of the efficient coupling ability of the DPDDPEDS surfactant with other non-ionic surfactants,an anionic surfactant-DPDDDFEDS in combination with a nonionic surfactant (LMA-EO-30) resulted in more stable colloidal dispersions due to the synergistic effect. Using this combination in the experiments provided particles stability throughout the reaction

All anionic surfactants like (DPDDFEDS) exhibited foam height and foam stability higher than non-ionic surfactant like (OP-EO-9) ethis means that the ionic surfactants have highly charged surface film on their foams, leads to increase its height and stability.

The use of surfactant mixtures, an anionic surfactant (DPDDPEDS) in combination with a nonionic surfactant (LMA-EO-30) resulted in more stable colloidal dispersions due to the synergistic effect. Using this combination in the experiments provided particles stability throughout the reaction.

Referance

1. Aguirreurreta, Z., de la Cal, J. C., Leiza, J. R.: Preparation of high solids content waterborne acrylic coatings using polymerizable surfactants to improve water sensitivity, Prog. Org. Coat. 112 (2017) 200-209, https://doi.org/10.1016/j.porgcoat.2017.06.028.

2. Zhao, J., Dai, C., Ding, Q., Du, M., Feng, H., Wei, Z., Zhao, M.:The structure effect on the surface and interfacial properties of zwitterionic sulfobetaine surfactants for enhanced oil recovery, RSC Adv, 5(18) (2015)13993-14001, https://doi.org/10.1039/C4RA16235H.

3. Xu, H., Xu, K., Wang, D.:Surface Chemical Properties and Micellization of Disodium Hexadecyl Diphenyl Ether Disulfonate in Aqueous Solution. J. Surf. Deterg.18 (6) (2015)1073–1080, https://doi.org/10.1007/s11743-015-1741-3.

4. Lovell, P. A., & Schork, F. J.: Fundamentals of emulsion polymerization. Biomacromolecules, 21(11) (2020) 4396-4441, https://doi.org/10.1021/acs.biomac.0c00769.

5. Yamak, H. B.: Emulsion polymerization: effects of polymerization variables on the properties of vinyl acetate based emulsion polymers. In Polymer science. IntechOpen.(2013), http://dx.doi.org/10.5772/51498.

6. El-hoshoudy, A. N. M. B.: Emulsion polymerization mechanism. Recent research in polymerization, 1(2018), http://dx.doi.org/10.5772/intechopen72143.

7. Gao, J., Penlidis, A.: Mathematical modeling and computer simulator/database for emulsion polymerizations. Prog. Polym. Sci, 27(3) (2002) 403-535, https://doi.org/10.1016/S0079-6700(01)00044-2.

8. Hu, X., Li, Y., He, X., Li, C., Li, Z., Cao, X., Somasundaran, P.: Structure–behavior–property relationship study of surfactants as foam stabilizers explored by experimental and molecular simulation approaches. J. Phys. Chem. B, 116(1) (2012) 160-167, https://doi.org/10.1021/jp205753w.

9. Bai, L., Liu, X., Jiao, T., Wang, Y., Huo, Y., Niu, J.: Surface properties and thermodynamic properties of micellization of mono-and di-tetrapropylene diphenyl ether disulfonates. Journal of Molecular Liquids, 244 (2017) 433-439, https://doi.org/10.1016/j.molliq.2017.09.033.

10. Amirianshoja, T., Junin, R., Idris, A. K., Rahmani, O.: A comparative study of surfactant adsorption by clay minerals. J. Pet. Sci. Eng, 101 (2013) 21-27, https://doi.org/10.1016/j.petrol.2012.10.002.

11. Manojlović, J. Ž.: The Krafft temperature of surfactant solutions. Thermal Science, 16 (2) (2012) 631-640, https://doi.org/10.2298/TSCI120427197M.

12. He, S., Xu, B., Zhang, Y.: Krafft Temperature, Critical Micelle Concentration, and Rheology of “Pseudo-Gemini” Surfactant Comprising Fatty Acid Soap and Bola-Type Quaternary Ammonium Salt. J, Surf. Deterg, 22(6) (2019) 1269-1277, https://doi.org/10.1002/jsde.12300.

13. Gao, X., Jasti, B. R., Huang, M., Wang, X., Mahalingam, R., Li, X.: Design and preparation of nanostructures based on Krafft point of nonionic amphiphiles for delivery of poorly water-soluble compounds. Inter. J. Pharm., 588 (2020), https://doi.org/10.1016/j.ijpharm.2020.119789.

14. Bai, L., Liu, X., Jiao, T., Wang, Y., Huo, Y., Niu, J.: Surface and Interfacial Properties of Mono and Didodecyl Diphenyl Ether Disulfonates. Tenside Surfactants Deterg. 55(4) (2018) 302-311, https://doi.org/10.3139/113.110573.

15. Zhao, J., Fan, J., Mao, J., Yang, X., Zhang, H., Zhang, W.: High performance clean fracturing fluid using a new tri-cationic surfactant. Polymers, 10 (5) (2018) 535, https://doi.org/10.3390/polym10050535.

16. Barquero, A., Leiza, J. R.; Evolution of the film properties of 3-methacryloxy propyl trimethoxysilane containing waterborne acrylic coatings during storage. J. Appl Polym. Sci., 138(6) (2021) 49796, https://doi.org/10.1002/app.49796.

17. ASTM D1331-89. ASTM International, West Conshohocken, PA 2001.

18. Negm, N. A., Elkholy, Y. M., Ghuiba, F. M., Zahran, M. K., Mahmoud, S. A, Tawfik, S. M.: Benzothiazol-3-ium cationic Schiff base surfactants: synthesis, surface activity and antimicrobial applications against pathogenic and sulfur reducing bacteria in oil fields. Journal of dispersion science and technology, 32(4) (2011) 512-518, https://doi.org/10.1080/01932691003756902.

19. Nedjhioui, M., Moulai-Mostefa, N., Morsli, A., Bensmaili, A.: Combined effects of polymer/surfactant/oil/alkali on physical chemical properties.Desalination, 185(1-3) (2005) 543-550, https://doi.org/10.1016/j.desal.2005.05.013.

20. Griffin, W. C. Classification of surface-active agents by ‘‘HLB’’. J Soc Cosmet Chem. 1 (1949) 311–325, https://doi.org/10.5458/jag.49.145.

21. Schick, M. J. Nonionic surfactants: physical chemistry. Surfactant Science Series, (1987) 438, ISBN 0-8247-7530-9.

22. Al-Sabagh, A. M., Azzam, E. M. S., El-Din, M. N.: Synthesis and evaluation of ethoxylated alkyl sulfosuccinates as oil spill dispersants. J. Dispersion Sci. techno., 29(6) (2008) 866-872, https://doi.org/10.1080/01932690701783119.

23. ASTM D1173-07. Standard test method for foaming properties of surface-active agents. ASTM International, West Conshohocken, (2007).

24. Denkov, N. D. Mechanisms of foam destruction by oil-based antifoams. Langmuir, 20(22) (2004) 9463-9505, https://doi.org/10.1021/la049676o.

25. Lima, M. T., Spiering, V. J., Kurt-Zerdeli, S. N., Brüggemann, D. C., Gradzielski, M., Schomäcker, R.: The hydrophilic-lipophilic balance of

carboxylate and carbonate modified nonionic surfactants. Colloid Surfaces A: Physicochemical Eng. Asp., 569 (2019) 156-163, https://doi.org/10.1016/j.colsurfa.2019.03.001.

26. Negm, N. A., Mohamed, A. S.: Surface and thermodynamic properties of diquaternary bola-form amphiphiles containing an aromatic spacer. J.Surf. Deterg., 7(1) (2004) 23-30, https://doi.org/10.1007/s11743-004-0284-z.
27. Hikota, T., Nakamura, M., Machida, S., Meguro, K.: Properties of aqueous solution of sodium cyclododecyl sulfate. J. Amer. Oil Chem. Soc., 48(12) (1971) 784-786, https://doi.org/10.1007/BF02609281.
28.Vautier-Giongo, C., Bales, B. L.: Estimate of the ionization degree of ionic micelles based on Krafft temperature measurements. J.Phys. Chem. B,107(23) (2003) 5398-5403, https://doi.org/10.1021/jp0270957.
29. Birdi, K. A. S.: Handbook of surface and colloid chemistry. CRC press ،(2008).
https://doi.org/10.1201/9781420007206
30. Reference chart for anionic and nonionic surfactant, Dow Surfactants Reference Chart, Dow chemical company. https://www.dow.com/content/dam/dcc/documents/en-us/catalog-selguide/119/119-01491-01-dow-surfactants-selection-guide.pdf.
31. Davies, J. T. K. Durham, HE Garrett, TG Jones, ASC Lawrence and DG Stevenson: Surface Activity and Detergency, Chem. Eng. Sci., 35 (1961) 250, https://doi.org/10.1016/0009-2509(62)80042-6.
32. AlYousef, Z. A., Almobarky, M. A., Schechter, D. S.: The effect of nanoparticle aggregation on surfactant foam stability. J. Colloid Interface Sci., 511 (2018) 365-373, https://doi.org/10.1016/j.jcis.2017.09.051.
33. Li, H. H., Imai, Y., Yamanaka, M., Hayami, Y., Takiue, T., Matsubara, H., Aratono, M.: Specific counterion effect on the adsorbed film of cationic surfactant mixtures at the air/water interface. J. Colloid Interface Sci., 359(1) (2011) 189-193, https://doi.org/10.1016/j.jcis.2012.08.044.
34. Zargartalebi, M., Barati, N., Kharrat, R.: Influences of hydrophilic and hydrophobic silica nanoparticles on anionic surfactant properties: Interfacial and adsorption behaviors. J. Pet. Sci. Eng., 119 (2014) 36-43, https://doi.org/10.1016/j.petrol.2014.04.010.
35. Zhang, Y., Pan, S., Ai, S., Liu, H., Wang, H., He, P.: Semi-continuous emulsion copolymerization of vinyl acetate and butyl acrylate in presence of AMPS. Iranian Polymer Journal, 23 (2014) 103-109, https://doi.org/10.1007/s13726-013-0205-8.