SYNTHESIS, CHARACTERIZATION AND STUDY OF SURFACTANTS EFFICIENCY IN THE DISPERSION (O/W) EMULSIONS

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Abstract

In the present study three classes of surfactants derivatives from benzillic acid were prepared. The prepared surfactants were characterized by FTIR-Infrared spectrophotometer and CHN analysis. The physical properties of the prepared surfactants were measured i.e. (pH, density, viscosity, color, freezing point and stability to hydrolysis). The efficiency of the prepared surfactants was studied with time and long side chain substituted. The hydrophilic-lipophilic balance (HLB) was calculated.

الخلاصة

تم تحضير ثلاث أنواع من المواد المنشطة للسطوح المشتقة من حامض البنزاليك والمستخدمة في تشتيت مستحلبات النفط في الماء (O/W). شخصت المواد المحضرة خلال الدراسة الحالية باستخدام مطيافية الأشعة تحت الحمراء والتحليل العناصر الدقيق (CHN)، كما تم قياس الخصائص الفيزيائية للمواد المحضرة والمتمثلة بـ (الدالة الحامضية، الكثافة، اللزوجة، اللون، درجة الانجماد والاستقرارية تجاه التحلل بعد إضافتها إلى المستحلب النفطي) فضلاً عن دراسة فعاليتها تجاه تشتيت اليقع النفطية مع الزمن وتأثير طول السلسلة الاليفاتية المعوضة على كفاءة التشتيت. كما تم حساب قيمة الموازنة بين المجاميع المحبة للماء والمحبة للدهون (HLB) باستخدام المعادلة (١).

Introduction

The common aromatic nuclei; benzene and naphthalene are not sufficiently hydrophobic to produce a high degree of field when they are combined with a sulphonic acid group. When however the aromatic uncles is substituted with one or more alkyl groups, which may be quite small, the amphipathic character of the molecules is greatly enhanced and in this class we fined may important surface-active agents [1a, 1 b].

The alkyl benzene sulphonates however are efficient detergents whene the alkyl group contains 10-14 carbon atoms. It is to be expected that the short-chain alkyl compounds would be much less effective than the long-chain ones in reducing the oil-solution interfacial tension, which would be a contributory factor in their being inferior demulsifier [2a, 2 b].

The most important of the synthetic surfactant carboxylate are the " Medialans " and " Lampeons ". The former, structures of which recall " Igepon T " , are sarcosine derivatives of general formula [R-CON (CH_3) $CH_2COO^-M^+$] in which M^+ is a simple ion such as Na^+ and R-CO is a group such as stearyl (C_{17}-CO) or olyl (C_{16}-CO) [3].

A surfactant is a chemical compound that affects the surface forces of a liquid or a solid in relation to other liquids, solids or gases. The surfactants generally consist of a molecule in which one end is hydrophilic (water-loving) and the other end is lipophilic (oil-loving) [4a, 4b].

A dispersing agent is used to promot the suspension of fine particles of a solid in a liquid. Hence, both surfactants and colloidal thickeners may fit the definition. A dispersing agent must wet the surface of the solid; yet, at the same

time, like an emulsifier, it must form a connecting like between particle and dispersing medium. The molecule is absorbed on the surface of the individual particles leaving exposed molecular ends which all have the same charge. Good dispersion in water borne paints provides better hiding, improved leveling and better color development and minimizes flooding and floating [5, 6].

In the present study the surfactants "alkyl benzillic acid salts" were used to treat oil in water (O/W) emulsions, which return for the Iraqi Ports Company and Najibia Electrical Station.

Experimental

Chemicals

1-bromo decane, 1-bromo dodecane, 1-bromo tetradecane, benzillic acid, aluminum chloride, sodium hydroxide, ethanol, water, urea, glue.

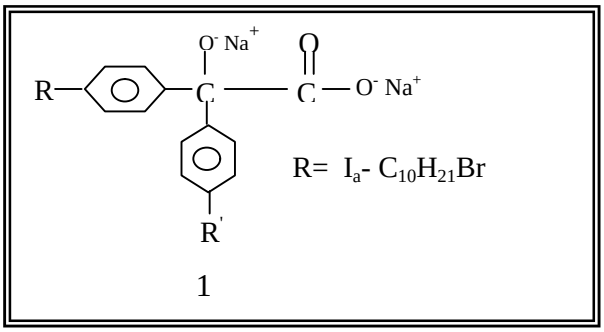
Instruments

1. FTIR-Infrared Spectrophotometer (8400S) made by (SHIMADZU) in the range (4000-400cm^{-1}) from Petrochemical Laboratories/ Basra.
2. Freezing Point Osmometer type (OSMOMAT 030) / College of Science-Basra University.
3. Elemental Analysis (CHN) / College of Science/ Cairo University.
4. pH-meter type (WTW) / College of Education/ Basra University [calomel and glass electrodes].
5. Density bottle glass.
6. Viscosity meter

Synthesis of Surfactants

2.28g (0.01mole) benzillic acid, 0.9g aluminum chloride and 4.24g (0.02mole) 1-bromo decane were dissolved and mixed with ethanol. After mixing, it was refluxed for (3h). The product was filtered and washed by water and hexane. The 4, 4'-didecayl benzillic acid was dried at (80^{0}C) in a vacuum oven. The 4, 4'-didodecayl benzillic acid (4.81g) [0.02mole] and 4, 4'-ditetradecayl benzillic acid (5.36g) [0.02mole] were prepared by the same procedure but the difference in the weight of alkyl halides[7].

The 4, 4'-dialkyl benzillic acid was treated with sodium hydroxide solution to adjust pH=7.7 and to obtain 4, 4'-dialkyl benzille sodium carboxylate (compounds 1). The surfactant was mixed with urea, glycine and glue to prepare dispersion.



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Synthesis of Dispersion

8g 4, 4'-dialkyl benzille sodium carboxylate, 5g urea, 4g glue and 3g glycine were dissolved in 70ml water and 10ml ethanol [20:80] [Solid: Liquid] to prepare the dispersion agents and used in treatment(O/W) emulsions. The measured properties of new surfactants are shown in Table (1).

Table (1): the values of physical properties from the prepared surfactants

Surfactant	pH	Density (g/cm^3)	Viscosity (Poice)	Color	Freezing point (^{0}C)	Stability time (hours)
I_a	7.7	1.2845	1.4643	Green	-12	1/2
I_b	7.7	1.3365	1.5110	Green-Yellow	-14	3/4
I_c	7.7	1.3871	1.5793	Yellow	-15	1

Viscosity Measurements

The ratio viscosity was calculated to the two liquids by viscometer and recorded the reological time to all water and the dispersed through equation (1).

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad \text{---------- (1)}$$

η_1, η_2: water and dispersed viscosity (Poice).
d_1, d_2: water and dispersed viscosity (g/cm^3) at 35^{0}C.
t_1, t_2: water and dispersed reological time (sec).

Stability Time

After preparing dispersion to all prepared surfactants in the present study was taken mixture of oil in water and put in glass container and the prepared surfactants (I_a, I_b and I_c) were sprayed respectively, with noticing the stability

time of emulsion through dispersing more ratio of oil with existing the foam of dispersion. According to above, more length aliphatic chains make more stability of emulsion as shown in Table (1).

Selection of Surfactants

The selection of surfactants depends on (HLB) which was calculated by equation (2). The prepared surfactants were used in (O/W) emulsion as shown in Table (2).This value then is an induction of the oil or water solubility of the product [6].

$$HLB = 20 * \frac{\text{Mole wt.EO} * \text{Moles EO}}{\text{Mole wt. of adduct}} \quad .....(2)$$

EO: The number of hydrophilic -lipoplilic groups.
HLB: Hydrophlic - lipophilic Balance.
Adduct: Molecular weight to the end compound

Table (2): the application of surfactants [3]

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

The (HLB) was calculated to the prepared surfactants as shown in Table (3).

Table (3): value of HLB for prepared surfactants

Surfactant	Value of HLB
I_a	12
I_b	14
I_c	16

Result and Discussion

The prepared surfactants (I_a, I_b and I_c) were confirmed by FTIR-spectra [8] taken in KBr and Figures (1-1) to (1-3) and Table (4).

Table (4): The absorption bands of surfactants, compounds (I_a- I_c)

Surfactant	Wave Number (cm^{-1})						
	C-H	C-C	C=C	C=O	O-H	C-O	C-H alkyl chain
I_a	3030ar 2925-2850al	1250	1580	1685	3400 - 3330	1150	720
I_b	3040ar 2925-2850al	1245	1590	1680	3400 - 3350	1130	730
I_c	3030ar 2930-2855al	1248	1585	1675	3400 - 3370	1120	725

ar: aromatic, al: aliphatic

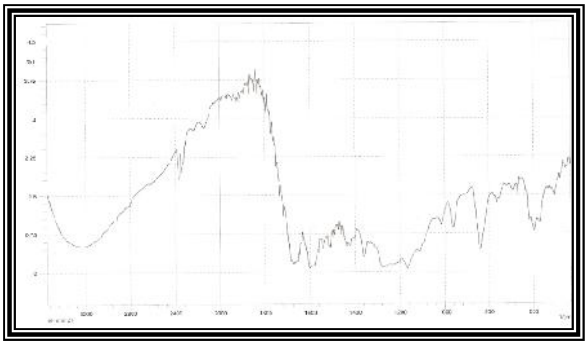

Figure (1-1): FTIR spectrum for I_a

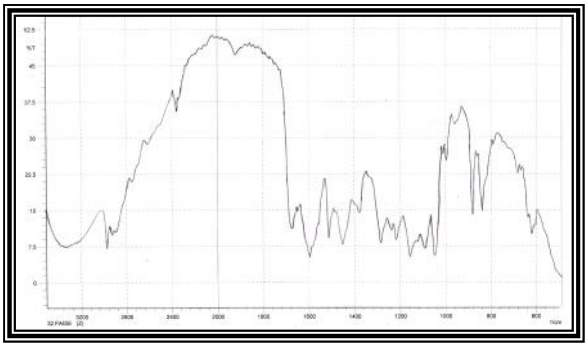

Figure (1-2): FTIR spectrum for I_b

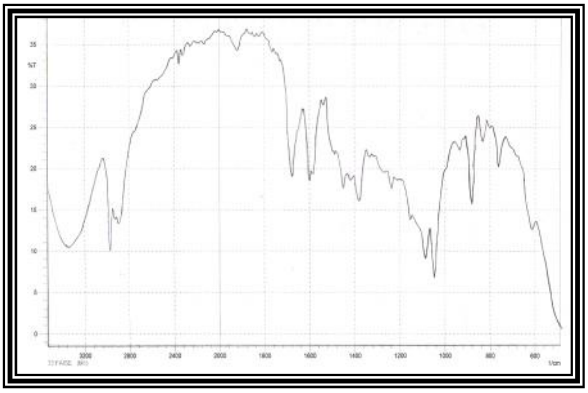

Figure (1-3): FTIR spectrum for I_c

The prepared surfactants were used to treat oil in water emulsions; the samples (O/W) were taken from the Iraqi Port Company and Najibia electrical Station poured in containers and added the prepared surfactants by spray of the prepared surfactants on the surface (oil spots). The activity of dispersion was increased with time due to the solubility of surfactants increased which was contained on two functional groups (hydrophilic and lipophilic), in addition to the ability of surface tension of liquid and broken the film of drops. The effect of long chain on dispersion was studied as shown in Table (5).

Table (5): the value of activity of prepared surfactants

Surfactant	Time (min)				
	10	30	50	70	90
I_a	35%	48%	60%	81%	95%
I_b	40%	52%	68%	83%	97%
I_c	49%	59%	75%	92%	99%

Table (5) shows the activity increase of prepared surfactants with increasing the alkyl chain length and time. The ratios were calculated by taking constant weight of oil before mixing with water. The water ratio was more than oil (1:100) [oil: water]. The hydrolysis time was calculated by dividing hydrolysied oil weight on constant oil weight and multiply the product in 100% at different time. The hydrolysis process of oil spots were increased with the length aliphatic chain.

The stability of prepared surfactants was increased by increasing the long chain after using in oil in water emulsions as shown in Table (1).

The value of HLB for the surfactants were calculated by equation (1) and used in the dispersion of (O/W) emulsion as shown in Table (3). All the group of prepared surfactants have constant value taken from many references to calculated the value of HLB (Hydrophilic-Lipophilic Balance). The calculated value of HLB to the prepared surfactants may be attributed to the range of oil in water emulsion depending on the values in Table (2).

The physical properties of the prepared surfactants were measured as shown in Table (1). The dispersion was prepared by addition of other material such as glue, glycin and urea. Glue is aviscus grad material used to increase the viscosity, liquefy the solution (anti gel) and stability of dispersion foam. Glycin is keeping the stability of foam, while Urea prevents glycin decomposing [7].

Elemental analysis shows the practical and theoretical values in Table (6). The practical values were increased theoretical values due to the prepared surfactants which have form viscous structure this leads to increase the surfactants weight.

Table (6): The values of CHN for Compounds (I_{a-c})

Compound	Practical Value %			Theoretical Value %		
	C	H	N	C	H	N
I_a	69.65	7.61	-	69.73	7.50	-
I_b	70.80	7.88	-	70.74	7.93	-
I_c	71.77	8.43	-	71.64	8.31	-

References

1. **a)** Bikerman, J.J., **1988**."*Surface Chemistry Theory and Applications*", Academic. Press Inc.Pub.N.Y. 2nd Ed. 155-157.

b) Ashok, K. and Bharti, S., **2007**. "*Innovations in Transdermal Drug Delivery: Formulations and Techniques*", Recent Patents on Drug Delivery & Formulation, 1, 23-36.

2. **a)** Bikerman, J.J., **1983**. "*Foams, Theory and Industrial Applications*", Rein hold. 169-174.

b) Hal, A., **2004**. "*Evaluation of IMO and Naval Type Bilge Cocktails*", President-MYCLEX Technologies Crop 1-9.

3. Shaw,D.J., **1992**. "*Introduction to Colloid and Surface Chemistry*", Butter Withers, London, 2nd. Ed. 206-213.

4. **a)** Paluson, B., **1994**." *Synthesis and Properties of New Anionic Surfactants*", J. Amer. Oil. Chem. Soc. 89. 556-563.

b) Golemanov, K. and Lips, A., **2006**. "*Latex-Particle-Stabilized Emulsions of Anti-Pancroft Type*", Langmuir. 22, 4968-4977.

5. Shelton, R.S., **1998**. "*Surface-active Properties of Novel Anionic Surfactants with Two Ammonia group*" J. Amer. Oil. Chem. Soc. 93. 556-564.

6. **a)** Pegiadou, S., **2000**. "*Synthesis, Characterization and Surface Properties of 1-N-L-tryptophan-glycerol ether Surfactants J. Surfactants and Detergents*, 30. 517-525.

b) Janus, P.F., and Mechiel, F., **2006** "*A Valuable Tool for Determination of Critical HLB Value of Emulsions*", APPS Pharm.Sci.Tech. 1- 7.

7. Eissa, A.M.F., **1993**. "*Preparation and surface active properties of oxypropylated diol mono esters of fatty acids with an amide oxime terminal group*", Grassy Aceites, 45. 306-308.

8. Hummel,D., **1968**. "*Identification and Analysis of Surface Active Agents*", London.