

Comparison studies of propylene oxide addition to phenyloctadecanol and phenyloctadecanoic acid and the surface activity studies of their sulphated products

By M.H.M. Ahmed

Chemistry Department, Faculty of Science, Benha University, Benha-Egypt

RESUMEN

Estudio comparativo de la adición de óxido de propileno a feniloctadecanol y ácido feniloctadecanoico y estudio de la actividad superficial de sus derivados sulfatados.

Se ha obtenido feniloctadecanol y ácido feniloctadecanoico vía reacción catalizada ácido de Lewis a partir de benceno y alcohol oleílico (60° C) o ácido oleico (80° C) respectivamente. Se ha llevado a cabo un estudio comparativo por adición de óxido de propileno a ambos sustratos en presencia de base (KOH) y ácido de Lewis (SbCl₅) como catalizadores. Se encontró que la hidroxipropilación de ambos sustratos a baja temperatura mediante catálisis ácido de Lewis es preferible a la catálisis básica. Se determinó la actividad superficial de los productos sulfatados. Los resultados mostraron que las muestras producidas a partir de alcohol (feniloctadecanol) tenían una mejor actividad superficial que las producidas a partir de ácido (ácido feniloctadecanoico). Por otro lado, las muestras producidas a partir de ambos sustratos utilizando catalizador ácido de Lewis tuvieron una actividad superficial mejor que las producidas con catálisis básica.

PALABRAS-CLAVE: Ácido feniloctadecanoico – Actividad superficial – Feniloctadecanol – Hidroxipropilación – Sulfatación.

SUMMARY

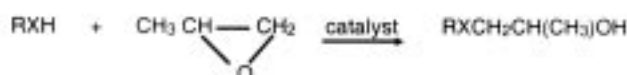
Comparison studies of propylene oxide addition to phenyloctadecanol and phenyloctadecanoic acid and the surface activity studies of their sulphated products.

Phenyloctadecanol and phenyloctadecanoic acid were produced via Lewis acid catalyzed reaction of benzene and oleyl alcohol (60°C) or oleic acid at (80°C) respectively. A comparison study was achieved for the addition of propylene oxide to both substrates in the presence of base (KOH) and Lewis acid (SbCl₅) catalysts. It was found that, the hydroxypropylation of both substrates at low temperature via Lewis acid catalyst is more preferable than via the base catalyst. The surface activity of the sulphated products was determined. The results revealed that, the samples produced from alcohol (phenyloctadecanol) show a better surface activity than that from acid (phenyloctadecanoic acid). On the other hand the samples produced from both substrates using Lewis acid catalyst have a better surface activity than that produced with the base catalyst.

KEY-WORDS: Hydroxypropylation – Phenyloctadecanol – Phenyloctadecanoic acid – Sulphation – Surface activity.

1. INTRODUCTION

Hydroxypropylation process is a reaction of propylene oxide with a compound containing active hydrogen.



where XH = OH, COOH, NH.....etc., and
R = long chain alkyl, aralkyl, alkyl phenol.....etc.

The hydroxyalkylation process is most technological important process in the production of nonionic surfactant. The choice of proper substrate, average degree of hydroxypropylation and type of catalyst can be reached to "tailor model". The tailor model is the compound produced according to its requested.

Since the hydroxypropylation reaction is a catalytic reaction [1], therefore it is largely affected by the type of catalyst used. The reactions of the fatty acid or alcohol with propylene oxide were reported [2-3]. The hydroxypropylated alcohol produced by the base catalyst is mainly monoester of propylene glycol [4].

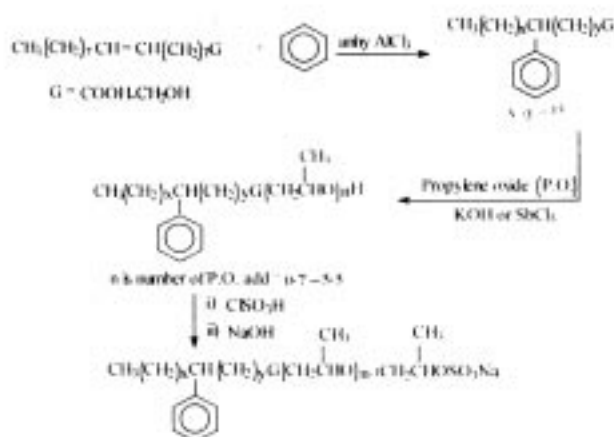
The insertion of propylene oxide unit in the hydrophobic chain has benefits effect, prolongs the hydrophobic fragment of surfactants or modifies their surface active properties [5,6]. So the solubility of hydroxypropylated products is poor and can be sulphated to increase their solubility [3]. The purpose of this work is to investigate the addition of propylene oxide to phenyloctadecanol and phenyloctadecanoic acid and study the influences of the catalysts on the surface active properties of the sulphated products. The sequence of the reaction was shown in Scheme 1. The results were studied from two points of view:

- 1) Addition of propylene oxide to the two substrates in the presence of base and acid catalysts.
- 2) Studies of the surface activity of their sulphated products.

2. EXPERIMENTAL

2.1. Preparation of phenyloctadecanol and phenyloctadecanoic acid [7,8]

Oleyl alcohol or oleic acid (1 mole) was mixed with benzene (6 mole) and the reaction mixture was



Scheme 1

stirred and heated (60°C in case of oleyl alcohol and 80°C in case of oleic acid) then anhydrous AlCl_3 (1 mole) was added in small portions through one hour. After complete addition of the catalyst, the reaction mixture was stirred for an additional one hour, then poured into (ice $\text{HCl} / \text{H}_2\text{O}$), extracted with chloroform, the solvent was distilled off (under vacuum) and the crude product was obtained (cf. Table I).

2.2. Synthesis of propylene oxide adducts

The hydroxypropylation was performed with the different catalysts, (they were applied in homogeneous phase): one is KOH and other is SbCl_5 .

Base catalyst

The hydroxypropylation was done as described in reference [9]. The number of propylene oxide mole added to one mole of the starting materials was calculated by method similar to that described in [10].

Lewis acid catalyst

The hydroxypropylation was completed as described in reference [11]. In an ice cooled 250 ml round flask fitted with a reflux condenser and magnetic stirrer calculated starting material and catalyst was

Table I
Characteristic parameters of the products

Product	Yield %	Boiling point	Characteristic state
phenyloctadecanol	69	188-194 $b_{0.3}$ [7]	viscous colourless oil
Phenyloctadecanoic acid	65	217-223 $b_{0.4}$ [8]	brown viscous oil

Table II
Reaction condition of hydroxypropylation process

Substrate	Catalysts		Reaction temp. °C	ADP
	type	conc. (mol %)		
Phenyloctadecanol	KOH	0.01-10	50-120	0.5-5.3
	SbCl_5	0.01-10	30-60	0.7-6.3
Phenyloctadecanoic acid	KOH	0.01-10	50-120	0.7-5.2
	SbCl_5	0.01-10	30-60	0.7-5.0

ADP: average degree of hydroxypropylation [10]

placed and the appropriated amount of propylene oxide was dropped. The desired temperature was achieved using thermostat, until the reaction complete. The unreacted propylene oxide was removed in vacuum. The mole of propylene oxide added was determined as maintained above (cf. Table II).

2.3. Synthesis of polyhydroxypropylated alcohol sulphates

Sulphation

It was completed as described in [6]. A typical procedure was: Hydroxypropylated alcohol (0.1 mole) was dissolved into 100 ml of CCl_4 , cooled, vigorously stirred and 10 mole % of chlorosulphonic acid was slowly dropped into the reaction mixture at a rate that the temperature remained below 5°C. After one hour of the stirring equal volume of cooled methanol was slowly added, the reaction mixture was neutralized with 40 % aqueous NaOH at 0°C. After 2 hours the solvent was distilled off; the final product was purified by dissolving several time into a hot mixture of methanol/ isopropanol.

$^1\text{H NMR}$ analysis

Nuclear magnetic resonance spectra were recorded on a Varian EM-390 spectrometer operating at 90 MHz. Deutero-chloroform was used as solvent and tetramethyl silane as internal standard. Chemical shifts are reported as (ppm) relative to tetramethyl silane.

2.4. Determination of the performance properties

The surface and interfacial tensions

The crude oily of the prepared compounds were used for the measurements in aqueous phase. The surface and interfacial tensions were measured with different surfactants concentrations at room temperature (25°C) using a Du-Nouy tensiometer (Kruss, type 8451) [12]. The cmc (critical micelle concentration) was determined by intersection in the curve of a relationship between surface tension (δ) and $\log [c]$.

Kraft point

Kraft point of the prepared surfactants was measured as the temperature at which 1 wt % dispersion becomes clear on gradual heating [13].

Wetting time

Was determined by immersing a sample of cotton fabric in 1 wt % aqueous solution of the surfactants [14].

Foaming height

Was measured according to [15]. A 25 ml solution (0.0 wt %) was shaken vigorously for 10 seconds in a 100 ml glass stoppered, graduated cylinder. The solution was allowed to stand for 30 seconds, and the foam height was measured.

Emulsion stability

The emulsion was prepared from 10 ml of a 20 mol aqueous solution of surfactant and 5 ml of toluene at 40°C. The emulsifying property was determined by the time it took for an aqueous volume separating from the emulsion layer to reach 9 ml counting from the moment of the cessation shaking [16].

RESULTS AND DISCUSSION

Preparation of starting materials: It was done in good yields according to [7,8] by Friedel-Crafts alkylation of oleyl alcohol or oleic acid to dry benzene in the presence of anhydrous $AlCl_3$. The characterization of the products is shown in Table I. The products were mixture of isomers (in case of oleic acid, there are 12 positions isomers with phenyl group at position 6-17 on the fatty acid chain [17], but with oleyl alcohol there are 5-phenyl isomer (at position 8-13 on the fatty alcohol chain) and a smaller amount of 17-phenyl isomer were formed [7]. The main isomers for both substrates are 9, 10 phenyl isomers.

3.1. Hydroxypropylation of the starting materials

It was carried out in homogeneous medium by using base catalyst (KOH) [9] and $SbCl_5$ [11]. The produced hydroxypropylated compounds were in the range 0.5-6.3 propylene oxide units (cf. Table II). The characteristic 1H NMR bands for the produced hydroxypropylated compounds was $\delta = 3.2-4.1$ [m, $-CH_2CH(CH_2)O$] and IR wagging vibration of $\delta_s CH_2$ of propylene glycol unit at 1376 cm^{-1} [18].

3.2. Hydroxypropylation studies

The hydroxypropylation was investigated at different temperature and catalyst concentration, the

Table III
Reaction velocity of hydroxypropylated phenyloctadecanoic acid and alcohol

Catalyst concentration	Acid (W.10 ²)	Alcohol (W.10 ²)	Temperature (°C)
KOH, 8.91 mole %	1.34* 0.15**	3.86* 0.44**	120
$SbCl_5$ 5 mole %	3.06* 0.612**	5.74* 1.15**	50

*ADP/min., **ADP/min. mole catalysts and (W) is virtual rate of hydroxypropylation.

results are tabulated (cf. Table III). The average degree of hydroxypropylation was plotted as function of the reaction time at a constant catalyst concentration and reaction temperature. The virtual reaction rate (W) was taken as the slope of the linear relationship, the results given in Table III. The alcohol shows rate approximately three time faster than the acid. Also in the both substrates the $SbCl_5$ shows a higher rate than KOH.

3.3. Sulphation

Sulphation of the products was done in good yields by method similar to that described in [6]. The disappearance of OH of propylene glycol in the IR spectra was recorded.

3.4. Surface activity

The surface properties of the sulphated products were investigated and the effect of the propylene glycol units on the surface properties has been clarified.

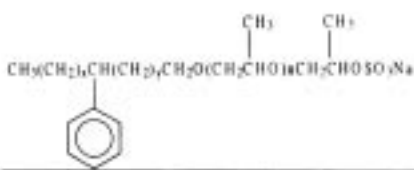
Surface and interfacial tension

Were measured at 1wt % surfactant concentration; the results are given in Table IV and V. The propylene glycol units has effect on the surface activity; as the number of propylene glycol increases [1.0 to 5.3], the surface tension of sulphated alcohol was increased from 33.0 to 46.3 mN/m and for the sulphated acid from 35.3 to 49.8 mN / m. The effect of the catalyst on the surface activity of the prepared sulphated compound was shown from the determination of the cmc [19]. It was determined by plotting the surface tension $[\sigma]$ against $\log [c]$; the values of cmc are shown in Table VI. The results of cmc for the hydroxypropylated phenyloctadecanol sulphate produced from $SbCl_5$ show a lower concentration and better surface activity in a comparison with that produced by KOH catalyst. The same tendency was observed for the hydroxypropylated phenyloctadecanoic acid sulphate. This can be attributed to the fact that the Lewis acid catalyst gave the narrow range distribution [5, 20]. Moreover, the hydroxypropylated

phenyloctadecanol sulphate produced from KOH shows a lower cmc and surface tension than that produced from hydroxypropylated phenyloctadecanoic sulphate by using the same catalyst. It is interesting to find a good relationship between surface tension

at cmc and propylene oxide units in the study range of the prepared compounds, in which sulphated group has not any effect on the relationship but it depends on the propylene oxide units (cf. Fig. 1). The constants of the relationship are given in Table VII.

Table IV
Surface properties of hydroxypropylated phenyloctadecanol sulphate (alcohol, KOH)

Sulphated products	n	Surface tension mN/m, 1 wt %		Interfacial tension mN/m 1 wt %	Foam height (mm) 1 wt %	Kraft point °C 1 wt %	Wetting time second 1 wt %	Emulsion min.
		SbCl ₅ *	KOH**					
	0.0	33.0	33.5	7.0	250	10	45	150
	1.0	33.5	35.5	8.0	240	12	43	145
	2.0	34.0	36.5	9.5	235	15	41	140
	3.0	35.0	42.0	11.0	230	17	39	135
	4.3	36.0	46.3	12.0	220	20	36	130

x + y = 15, *hydroxypropylated sulphate produced via Lewis acid catalyst and **that produced via base catalyst.

Errors of measurements were:

Surface and interfacial tensions = ± 0.1 dynes/cm.

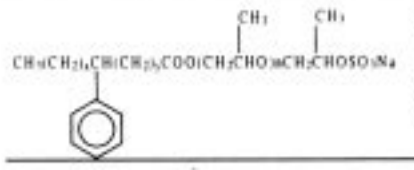
Kraft point = ± 1°C

Foam height = ± 2 mm.

Wetting time = ± 1 sec.

Emulsion = ± 1 min.

Table V
Surface properties of hydroxypropylated phenyloctadecanoic acid sulphate

Sulphate products	n	Surface tension mN/m 1 wt %		Interfacial tension mN/m 1 wt %	Foam height (mm) 1 wt %	Kraft point °C 1 wt %	Wetting time second 1 wt %	Emulsion min.
		SbCl ₅ *	KOH**					
	0.0	33.5	35.3	8.0	230	14	49	140
	1.0	34.0	36.8	9.0	220	13	46	135
	2.0	35.5	43.2	11.0	215	15	44	130
	3.0	37.5	46.2	12.0	210	17	41	125
	4.2	41.5	49.8	14.0	200	18	40	125

x + y = 15, *hydroxypropylated sulphate produced via Lewis acid catalyst and **that produced via base catalyst.

Errors of measurements were:

Surface and interfacial tensions = ± 0.1 dynes/cm.

Kraft point = ± 1°C

Foam height = ± 2 mm.

Wetting time = ± 1 sec.

Emulsion = ± 1 min.

Foaming property

The results are given in Table IV and V, indicating that the increase in the hydroxypropylene chain length causes a decrease in the foam height; the hydroxypropylated samples produced from acid substrate

has lower foam height than that from alcohol for the same number of propylene oxide units [5].

Wetting property

The wetting time for hydroxypropylated phenyloctadecanol and for phenyloctadecanoic acid

Table VI

cmc and δ (surface tension at cmc) values for hydroxypropylated phenyloctadecanol and phenyloctadecanoic acid sulphate. The standard deviation of δ was found to be ± 0.5

APD	cmc [mol/l]	δ [mN/m]	ADP	cmc [mol/l]	δ [mN/m]
Hydroxypropylated phenyloctadecanol sulphate					
KOH					
1.0	0.0193	34.63	0.9	0.0182	33.85
2.0	0.0237	35.90	2.0	0.0205	34.70
3.0	0.0272	37.83	3.0	0.0253	36.52
4.0	0.0372	38.87	4.0	0.0308	38.05
Hydroxypropylated phenyloctadecanoic acid sulphate (KOH)					
KOH					
2.0	0.028	37.10	2.0	0.0261	35.43
3.0	0.0329	38.60	3.0	0.0275	37.14
4.0	0.0392	39.76	4.0	0.0324	38.56

Table VII

Constants of the relationship of propylene oxide units and δ surface tension at cmc for the prepared sulphated compounds

Hydroxypropyl Sulphated Compounds	Catalyst	α	S	SD	I
Phenyloctadecanol	KOH	0.993	1.465	0.258	33.145
Phenyloctadecanol	SbCl ₅	0.990	1.442	0.312	32.175
Phenyloctadecanoic	KOH	0.997	1.330	0.138	34.497
Phenyloctadecanoic	SbCl ₅	0.998	1.565	0.118	32.450

(α) is correlation coefficient; (S) is slope; (SD) is standard deviation; and (I) is intersection

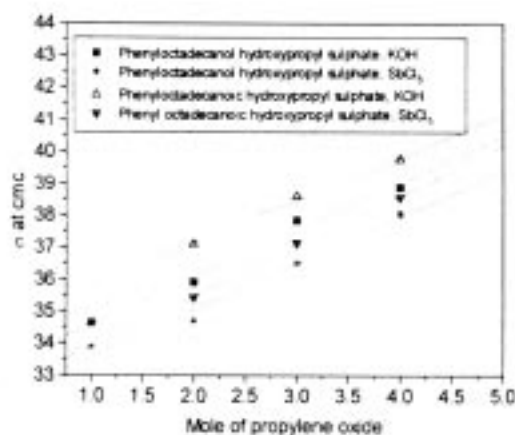


Figure 1

Relationship between mole of propylene oxide and surface tension at cmc for prepared hydroxypropyl sulphated compounds.

sulphate has the same tendency (Tables IV and V). When increasing the number of hydroxypropylene unit in the molecule, the wetting time was decreased; this means that, the propylene unit inserted in the molecule has an effect on this property. The presence of hydroxypropylene units improves the wetting of aqueous solutions of these compounds [3].

Kraft point and emulsion properties

For both of the hydroxypropylated compared compounds, the Kraft point has the same tendency (Tables IV and V). It was increased by increasing the number of propylene oxide units in the molecules. The reverse trend was obtained for the emulsion property [21].

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