

Preparation and surface active properties of oxypropylated diol monoesters of fatty acids with an amide oxime terminal group.

By A.M.F. Eissa, A.A. Mahmoud and A.A. El-Sawy
Chemistry Depart., Faculty of Science, Benha University, Egypt.

RESUMEN

Preparación y propiedades de tensión superficial de diol monoésteres oxipropilados de ácidos grasos con un grupo terminal amido oxima.

Se ha utilizado un aceite no comestible de producción local, denominado, aceite de salvado de arroz (R.B.O.) como materia prima para la preparación de nuevos tensioactivos no iónicos.

Se prepararon diol monoésteres oxipropilados de ácido linoleico y ácidos grasos de aceite de salvado de arroz. También se obtuvieron los derivados de amido oxima. Se midieron las propiedades de tensión superficial de estos compuestos. Bajo condiciones neutras las amido oximas sirvieron como tensioactivos no iónicos y sus propiedades fueron similares a los de otros monoésteres oxipropilados.

PALABRAS-CLAVE: Aceite de salvado de arroz — Tensioactivo no iónico (preparación) — Tensión superficial (propiedades).

SUMMARY

Preparation and surface active properties of oxypropylated diol monoesters of fatty acids with an amide oxime terminal group.

Locally produced non-edible oil, namely, rice bran oil (R.B.O.) was utilized as starting materials for preparing new nonionic surfactant. Oxypropylated diol monoesters of linoleic and rice bran oil fatty acids were prepared. Also amide oxime derivatives were obtained. Surface active properties of these compounds were measured. Under neutral condition amide oximes served as nonionic surfactants and their properties were similar to other oxypropylated monoesters.

KEY-WORDS: Nonionic surfactant (preparation) — Rice bran oil — Surface active (properties).

1. INTRODUCTION

The most important category of fatty nonionic surfactants are polyoxyethylene and polyoxypropylene derivatives of fatty alcohols, acids, amines and amides. Other examples of nonionic surfactants are fatty alkanolamides, anhydrohexitol derivatives, glycol, glycerol, and sugar esters. They can function in the presence of large quantities of electrolytes, in very hard water or acidulated water, or in the presence of various metal ions, and they can remove soil under a variety of conditions.

Locally produced non-edible oils, namely, rice bran and castor oils were utilized as starting materials for preparing nonionic surfactants by reacting with ethylene and propylene oxides (1) (2). In an extension of our interest in the synthesis and study of the surface activity of the nonionic surfactants derived from crude rice bran oil (3), a novel group of surfactants possessing good surface properties and expected to have chelating properties was prepared (4).

2. EXPERIMENTAL

2.1. Crude rice bran oil

This oil was supplied by the Alexandria Company for extraction and hydrogenation of oils. The specifications are given in (Table I).

Table I. Specification of crude rice bran oil

Saponification value	176
Iodine value	102
Acid value	70

2.2. Hydrolysis of the crude rice bran oil

The procedure described by El-Sawy (5) was followed. The obtained mixed acid was analysed by G.L.C. and its composition is given in (Table II).

Table II. Fatty acid composition of crude rice bran oil*

Acid	Percentage mass %
Palmitic	17.6
Stearic	0.9
Oleic	50.1
Linoleic	27.1
Linolenic	2.2

* The molecular weights of acids in R.B.O. are considered as oleic (molecular weight of oleic = 282).

2.3. Oxypropylation of 1,4-butane and 1,6-hexane diols

The procedure described in (6) was followed in which the diols, propylene oxide and potassium hydroxide were charged to the propoxylation apparatus.

2.4. Preparation of oxypropylated diol ester of fatty acids: [formation of (I)]

The general procedure for preparing oxypropylated diol monoesters consisted of reacting oxypropylated diol with boric acid, esterifying the resulting borate with fatty acids using *p*-toluensulphonic acid as catalyst, and selectively hydrolysing with a minimum amount of water. A typical preparation was described according to ref (6).

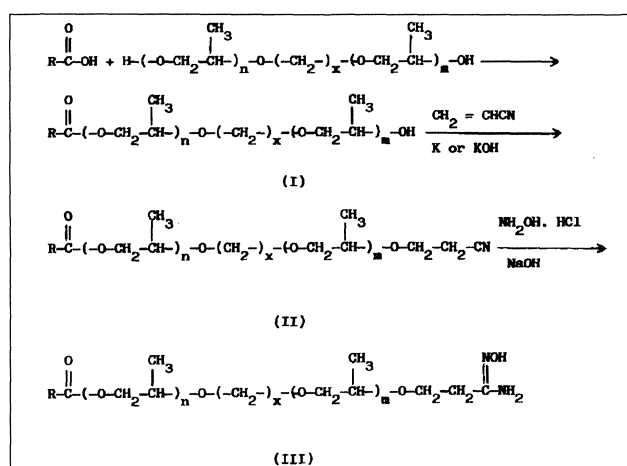
2.5. Preparation of alkyl (oxypropylene) oxypropionenitrile: [formations of (II)]

After metallic potassium (0.1g, 5 mmole) was dissolved in monoester (50 mmole), acrylonitrile (57 mmole) was dropped carefully at 30°C and the mixture was stirred at this temperature for 24 hr.

After neutralization by hydrochloric acid, water (100 ml) was added and the reaction mixture was extracted with methylene chloride (100 ml, 4 times). After the extracts were combined and dried with MgSO₄, the evaporation of the solvent gave crude product which was confirmed by spectral data (4).

2.6. Preparation of alkyl (oligo (oxypropylene) oxypropionamide oxime): [formation of (III)]

Hydroxylamine hydrochloride (3.5 g, 51 mmole) in methanol (30 ml) was added to sodium hydroxide (2.11 g, 50 mmole) in methanol (30 ml) at °C, and insoluble solids were separated off by filtration. To this filtrate (20 mmole) of nitrile in methanol (40 ml) was dropped and the mixture was stirred at room temperature for 24 h. (pH 5-7 under these conditions). After filtration and subsequent evaporation of the filtrate, methylene chloride (50 ml) was added to the residue. Insoluble solids were filtered off again, and the crude product was obtained by the evaporation of filtrate. The product was confirmed by its spectral data.



- a) $(n+m) = 15$, $x = 4$ or 6 and $R =$
Alkyl group of linoleic acid or alkyl group of mixed acids
(palmitic, oleic and linoleic).
- b) $(n+m) = 20$, $x = 4$ or 6 and $R =$
Alkyl group of linoleic acid or alkyl group of mixed acids
(palmitic, oleic and linoleic).

2.7. ¹H-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.

2.8. Evaluation of the products obtained

Surface tension. Surface tension of the prepared compounds were measured using a Du-Nouy tensiometer at room temperature.

Foaming property. Was examined by standard method (7).

Cloud point. The cloud point, a measure of inverse solubility characteristic of nonionic surface active agent, was determined by gradually heating 1% solution in controlled temperature bath and recording the temperature at which the clear, or nearly clear, solutions became definitely turbid. The reproducibility of this temperature was checked by cooling the solutions until they became clear again (8).

Emulsion stability. Emulsion was prepared from 10 ml of 20 mmole aqueous solution of the surfactant and 5 ml of toluene at 40°C. The emulsifying properties was determined as the time (in min) from cessation of shaking taken for 9 ml of an aqueous layer to separate from the emulsion (9).

3. RESULTS AND DISCUSSION

The availability of propylene oxide at a relatively low price coupled with its ease of reaction to form polyoxypropylene glycols open the way to an almost unlimited number of relatively inexpensive base materials for the synthesis of nonionic surface active agents. In the present study monoesters of a variety of oxypropylated diols were prepared. Esterification of the borate of oxypropylated diols, obtained by reaction of boric acid and oxypropylated diols, with the chosen fatty acid gave monoester in 80-85% yield. Free fatty acid were removed by passage through an alkaline silica gel bed. TLC showed them to be pure.

3.1. Surface active properties of oxypropylated diol monoesters of fatty acids

The monoester may be expected to be a more valuable detergent and surface active agent than the diester, or than a mixture of monoester, diester, and polyethylene glycol. In any event the properties of a reasonably pure monoester preparation would be of interest.

Surface tension. The surface tension of the prepared esters are shown in Table III. It is evident that the surface tension increases with the increase in the molecular weight of hydrophobic moiety (10).

Foaming properties. Nonionic surfactants, generally are rated as low to moderate foamers (7). The surfactants obtained from linoleate and R.B.O. have moderate to low foam respectively. The foam height decreases by increasing the number of propenoxy groups per hydrophobic molecule (Table III).

Table III. Surface active properties of the prepared surfactants α -oxypropylated monoesters

Type of ester	Cloud point "°C" 0.1%	Surface tension "mN/m" 0.1%	Foam height "mm" 0.1%	Emulsifying stability "min:sec" 0.5%
Linoleate*	56	34	200	8:46
R.B.O.*	70	41	100	16:14
Linoleate**	68	38	100	8:6
R.B.O.**	80	42	40	15:22

R.B.O.= Rice Bran Oil.

* = Monoester of oxypropylated 1,4-butane diol (15 mole propylene oxide).

** = Monoester of oxypropylated 1,6-hexane diol (20 mole propylene oxide).

Emulsion stability. Studies are still being carried out on the utilization of surfactants in emulsion formation which is of immense importance to technological development. It was proved that the emulsifying stability of oxypropylated monoester especially those of R.B.O. exhibit a good emulsifying properties (Table III) which make them of choice in pesticide and cosmetic formulation.

Cloud point. A very important factor in making the most efficient use of nonionic surfactants in aqueous system is an understanding of property called cloud point. The data (Table III) show that the cloud point increases by increasing the number of propenoxy groups per hydrophobic molecule. The cloud point of the prepared surfactants is less than 100°C.

Table IV. Surface active properties of the prepared surfactants β -amide oxime derivatives

Type of ester	Cloud point "°C" 0.1%	Surface tension "mN/m" 0.1%	Foam height "mm" 0.1%	Emulsifying stability "min:sec" 0.5%
Linoleate*	75	41.5	120	7:31
R.B.O.*	83	44.0	80	15:13
Linoleate**	80	44.0	73	2:00
R.B.O.**	89	45.5	40	13:06
C ₁₂ E ₄ AO*	22.5	31	120	-

*=Amide oxime of oxypropylated 1,4-butane diol monoester (15mole)

**=Amide oxime of oxypropylated 1,6-hexane diol monoester (20mole)

*=Amide oxime of oxyethoxylated fatty alcohol

C₁₂E₄AO = CH₃(CH₂)₁₀CH₂O(CH₂CH₂O)₄CH₂CH₂C-NH₂

||
NOH

3.2. Surface active properties of amide oxime surfactants. (Table IV)

These amide oximes acted as cationic surfactants under acidic conditions and as nonionic ones under neutral and basic condition (4). Surface active properties of the prepared compounds were measured under neutral conditions as nonionic ones. They possess good properties and afford much information to application of amide oximes to ion-flotation systems.

It is very interesting to know that, by modification of the terminal OH-group of oxypropylated diol monoester (through formation of nitriles, then amide oxime), the improvement of surface properties compared with parent compounds as following:

- Decrease in foam height, a feature of end-blocked nonionics is low foaming or antifoaming properties but especially showed good foam stability (11).
- The cloud point increases by increasing the number of propenoxy groups per hydrophobic molecule. The cloud point of the amide oxime surfactant type is higher than of oxypropylated monoester. (Table III and IV).

3.3. The H¹-NMR (CDCl₃) spectrum of amide oximes

The protons are assigned as follows:

Methyl group at 0.89 (t) ppm; methylene groups (in alkyl chain) in the 1.16-1.6 (m) ppm region; methylene of (O-C-CH₂-C(=NO)-N at 2.3 (t) ppm; methylene group of (-O-CH₂-C-C(=N-O) at 3.4 (t); (OCH(CH₃)-CH₂-O-and(alkyl chain)-CH(OPO)-CH₂-O) in the 3.49-3.8 (br.m) ppm region and (broad 3H of C-C(=N-OH)-NH₂) in the 4.4-5.2 ppm region.

REFERENCES

1. Tawfik M. Kassem., El Dib, F. and El-Sawy A.A. (1986).- "Nonionic surface active agents from Egyptian non-edible (fats) oils".- Tenside Detergents **23** (4) 178-180.
2. El-Sukkary, M.M.A., El-Dib, F., El-Sawy, A.A. and El-Ashry, S.H. (1986).- "Preparation of nonionic surfactants from rice bran oil".- Hungarian Journal of Industrial Chemistry **14** (2) 219.
3. El-Sukkary, M.M.A., El-Sawy, A.A. and El-Dib, F. (1987).- "Synthetic detergents from crude rice bran oil".- Hungarian Journal of Industrial Chemistry **15**, 317.
4. Arki, M., Tomomichi, O. and Mitsuo, O. (1988).- "Preparation and surface active properties of alcohol ethoxylates with an amide oxime terminal group".- J. Am. Oil Chemists' Soc. **65**, 1821.
5. El-Sawy, A.A. (1989).- "Synthesis of sucrose esters from rice bran oil fatty acids".- Grasas y Aceites **40**, 382-384.
6. El-Sawy, A.A., Mahomoud, A.A. and Shaker, N.O. (1990).- "Preparation and surface properties of oxypropylated diol monoester of fatty acids".- J. Serb. Chem. Soc. **55**, 395-400.
7. Hans, S. (1988).- "Foaming of nonionic surfactant solutions: effect of surfactant concentration and temperature.- J. Am. Oil Chemists' Soc. **65**, 1821.
8. Cohen, A.W. and Rosen, M.J. (1981).- "Wetting properties of nonionic surfactants".- J. Am. Oil Chemists' Soc. **58**, 1062-1065.
9. El-Sawy, A.A., Essawy, S.A., El-Sukkary, M.M. and Eissa, A.M.F. (1992).- "Surfactants from 2-hydroxy fatty acids".- Hungarian Journal of Industrial Chemistry **20**, 25-28.
10. El-Sawy, A.A. (1992).- "Synthesis and properties of amphoteric surfactants derived from aspartic acid".- Hungarian Journal of Industrial Chemistry **20**, 29-32.
11. Arki, M., Ko-ichi, A. and Mitsuo, O. (1987).- "Surface active hydroxamic acids".- J. Am. Oil Chemists' Soc. **64**, 1040.

(Recibido: Diciembre 1993)