

EVALUATION OF POLYGLYCEROL ESTERS
AND THEIR SULFATED DERIVATIVES

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ABSTRACT

Product composition of polyglycerol esters, prepared from a direct alkaline polymerization of glycerol followed by esterification with different fatty acids, has been examined. The polyglycerol esters were further sulfated to produce the corresponding sulfated derivatives. The hydrophile-lipophile balance (HLB) of polyglycerol esters were determined. The surface active properties of the sulfated derivatives were given. It was found that polyglycerol esters became less hydrophilic as the chain length of the aliphatic acid used in esterification was increased. The high HLB values of the laurate and myristate esters suggest their possible use as wetting agents, while the other prepared esters may be useful as emulsifying agents. The sulfated derivatives, however possess excellent foaming power. Those of medium chain length of the hydrophobe may be promising in applications where emulsification wetting , and foaming are desired.

Delta J. Sci. 12 (3) 1988
Evaluation of Polyglycerol

INTRODUCTION

Polyglycerol esters (PGE) are versatile nonionic surfactants industrially prepared and commercially available as food, cosmetic and pharmaceutical emulsifiers (McIntyre, 1979 ; Osipow and Rosenblatt, 1967). The main industrial production process (Stewart and Hughes, 1972) is based on direct esterification of fatty acids with polyglycerol in the presence of alkaline catalyst at elevated temperatures. The products are composed of a mixture of predominantly linear glycerol polymer esterified with fatty acids (Hemker, 1981 ; Babayan and Lehman , 1972). Varying polymer length and type or degree of esterification of the PGE provides the basis for utility in product application by enabling the ester to acquire a desired hydrophile-lipophile balance (HLB) (McIntyre, 1979).

The sulfation of PGE will have of course considerable effect of these compounds and they may behave as anionic and nonionic surface active agents. Sulfated derivatives may be simply made by reaction of sulfuric acid with the polyglycerol ester to produce the corresponding sulfated products.

Although random studies (Babayan, 1971 ; Garti et al., 1981 ; Garti and Aserin, 1982 ; Kaufman and Garti, 1982) have been carried out on the preparation, properties,

Delta J. Sci. 12 (3) 1988

Shaker et al.

structure and application of polyglycerol ester, however information concerning their sulfated derivatives are scarce.

The purpose of the present study has been to examine the degree of hydrophilic activity of some fatty acid polyglycerol esters and the surface active properties of their sulfated derivatives : Medium and long-chain saturated , unsaturated, epoxy and hydroxy acid esters were first prepared and partially characterized. These esters were further sulfated and the products evaluated with respect to surface-active properties including wetting, foaming and emulsification power.

MATERIAL AND METHODS

Materials:

Polymerization of glycerol:

Polyglycerol was obtained by heating dry glycerol to 150°C for about 30 min under an atmosphere of N₂ to exclude air. Powdered NaOH was added with continuous stirring and the temperature of the mixture was raised to 250-280°C. Stirring was continued for 2 hrs. and then cooled.

Esterification of polyglycerol:

Esterification was simply made by heating the free

Delta J. Sci. 12 (3) 1988

Evaluation of Polyglycerol

fatty acid with polyglycerol at 220°C under a stream of nitrogen until the acid value of the product was less than 2.

Sulfation of polyglycerol esters

Concentrated sulfuric acid was added dropwise to the polyglycerol ester with continuous stirring. The temperature was maintained below 30°C for 30 mins. The mass was washed with sodium sulphate solution (15%) until free from acid and neutralized to pH 6.7 - 7.0.

Methods:

Polyglycerol esters were analysed for their acid, saponification and hydroxyl values according to standard methods of analysis (A.O.C.S. 1979 ;A.O.T.A.C. 1980). The HLB values were computed from the Griffin formula (Griffin, 1949, 1954) The fundamental surface active properties of the sulfated derivatives including surface and interfacial tensions, wetting, foaming and emulsifications were evaluated according to procedures described previously (Sadek and Ali, 1984).

RESULTS AND DISCUSSION

The polymerization of glycerol involves the α -hydroxyl groups of two glycerol molecules to form an ether linkage with release of a water molecule. The resulting product form a

Delta J. Sci. 12 (3) 1988

Shaker et al.

whole family of polyglycerols containing from 3 to 32 hydroxyl groups (McIntyre 1979).

Some of the prepared polyglycerol esters of varying fatty acids are summarized in table 1. Only negligible amounts (0-1.4 %) of fatty acids remained unreacted in some products. The HLB was directly related to the saponification value of the ester and values ranging from 3.2 to 7.4 were observed. The hydrophilic nature of polyglycerol esters increased with the decrease of the chain length of the fatty acid from C₁₈ (stearic) to C₁₂ (lauric). The presence of a double bond in the fatty acid moiety slightly increased the hydrophilic properties of the product.

The utility of most polyglycerol esters is dependent upon their hydrophilic - lipophilic properties : the higher the HLB value, the greater is the hydrophilic property (McIntyre 1979). Therefore, the high HLB values observed for the laurate and myristate esters suggests their use as wetting agents, while the other prepared esters may be useful as emulsifying agents.

Manufacturers and formulators of flavors find the oleates with HLB value above six to be effective solubili-

Delta J.Sci. 12 (3) 1988
Evaluation of Polyglycerol

zers and carriers of essential oils and essences. The pharmaceutical and cosmetic manufacturers have utilized these compounds as part of emulsifier systems, thickening agents and opacifiers. Polyglycerol oleates have been tested as therapeutic agents and interest has been shown for their use as replacement for bile salts in some malabsorption syndromes (McIntyre 1979).

The sulphated polyglycerol esters were shown to be efficient surface-active agents (table 2,3). They generally had a remarkable surface-tension-lowering effect. All the sulfated esters had good wetting power. The laurate and myristate were the most efficient wetting agents. Except the myristate and epoxystearate all the esters possess excellent foaming power.

Since the longer-chain monoesters of several polyglycerols have been found (Babayan,1971) to be useful as dispersants or emulsifiers in diverse applications, the emulsifying power of the sulfated polyglycerol esters was evaluated. Table 3 shows clearly that all these products had great bearing on the emulsifying property and stability of the formed emulsions. The stearates, oleates and ricinoleates were the most efficient emulsifiers. The product prepared from soapstock mixed fatty acids

Delta J. Sci. 12 (3) 1988

Shaker et al.

possess excellent foaming and emulsifying properties and represents a sample which can be produced from relatively cheap source materials and low grade fatty acids of possibly considerable economic value.

The combined surface activity of these compounds allow them to be used in cosmetics and as auxiliary agents in the fiber, plastic, leather and many other industrial applications.

Delta J. Sci. 12 (3) 1988
Evaluation of Polyglycerol

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Table 1
Esterification of Polyglycerol with Different Fatty Acids.

Fatty acid	A.V.	F.F.A. %	S.V.	E.V.	H.L.B. value	OH value
Lauric	0	0	163.1	163.1	7.4	221.4
Myristic	0	0	159.5	159.5	7.2	218.3
Palmitic	1.4	0.7	153.1	151.6	5.9	196.5
Stearic	2.9	1.4	148.6	145.7	5.8	186.3
Monooxy	0	0	151.8	151.8	4.6	174.7
Oleic	1.4	0.7	142.9	141.4	6.2	184.8
Ricinoleic	1.0	0.5	179.2	158.1	3.2	172.6
Soapstock fatty acid.	0	0	139.9	139.9	3.6	178.8

Mole ratio of polyglycerol: fatty acid 5:1.

Reaction period: 1 hr.

Temperature : 220°C.

Polymerization period: 2 hrs.

Table 2
Surface Active Properties of Different Sulfated Fatty
Polyglycerol Esters.

Esters of	Surface tension	C.M.C.	Foaming		Wetting (min)
	(dyne/cm) 0.1/100 ml		[g%]	0 min	
Lauric	32.0	0.309	380	80	0.5
Myristic	30.5	0.316	60	90	1.0
Palmitic	31.0	0.323	220	180	3.0
Stearic	30.0	0.316	160	6	6.0
Monoepoxy stearic	33.0	0.323	19	7	11.0
Oleic	32.5	0.281	200	16	2.0
Ricinoleic	33.5	0.316	260	30	5.0
Soapstock F.A.	35.0	0.288	180	20	4.0

Table 3

Interfacial Tension and Emulsification Property of
Different Sulfated Fatty Polyglycerol Esters.

Esters of	Interfacial tension (dyne/cm) 0.1 /100ml	Emulsification					
		0	-	1hr	>24hr		
Lauric	13.3	20	e	5	e	5	e
		0	O	0	O	0	O
Myristic	12.5	20	e	6	e	6	e
		0	O	0	O	0	O
Palmitic	12.6	20	e	6	e	6	e
		0	O	0	O	0	O
Stearic	10.9	20	e	7	e	7	e
		0	O	0	O	0	O
Monc poxy stearic	13.2	20	e	5	e	5	e
		0	O	0	O	0	O
Oleic	11.2	20	e	7	e	7	e
		0	O	0	O	0	O
Ricinoleic	11.3	20	e	7	e	7	e
		0	O	0	O	0	O
Soapstock F.A.	10.5	20	e	8	e	8	e
		0	O	0	O	0	O

e : emulsion.

O : oil.

