Preparation and Surface-Active Properties of Polyoxyethyleneglycol (600) Monoesters of Fatty Acids

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ABSTRACT AND SUMMARY

Polyoxyethyleneglycol (PEG-600) monoesters of undecylenic, lauric, myristic, palmitic, stearic, oleic, ricinoleic and 12-hydroxystearic acids were prepared in 80-85% yield by reacting PEG with boric acid, esterifying the resultant borate with fatty acid, and selectively hydrolyzing the borate ester; their surface active properties were evaluated. Increase in acyl chain length increased the surface tension. The presence of a double bond or hydroxyl group in C_{18} series improved the wetting and emulsifying properties. Unsaturation in the fatty acid chain reduced the foaming power.

INTRODUCTION

Polyoxyethyleneglycol (PEG) monoesters of fatty acids, being low foamers and good emulsifiers, find extensive use in textile industry and pesticide formulations and also in cosmetic preparations (1). PEG fatty acid esters are prepared by either ethoxylation (2,3) or esterification (4). The latter process is safer and more easily controllable as desired. Even here, considerable proportions of diesters are formed unless a large excess of glycol is employed (4,5). Pure monoester can be readily obtained by forming a borate with glycol and esterifying with a fatty acid (6). This route has been applied earlier for the preparation of a variety of monoesters of ethylene glycol as intermediates for pure mixed diesters (7). In the present investigation pure PEG (600) monoesters of a variety of fatty acids have been prepared by the same route and their surface-active properties have been evaluated.

EXPERIMENTAL PROCEDURES

Materials

Lauric, myristic, and palmitic acids (The British Drug Houses, Ltd., England) were fractionally distilled as their methyl esters. Gas liquid chromatography (GLC) showed that laurate contained 3% caprate; myristate contained 2% laurate; and palmitate contained 3% myristate, as contaminants. GLC pure undecylenic acid was prepared by pyrolysis of castor oil and ester fractionation (8). Stearic acid (95% pure) was obtained from technical stearic acid by ester-fractionation. Oleic acid (96% pure) was prepared by urea adduction of mixed fatty acids of kokum butter (*Garcinia indica*) followed by distillation as methyl esters. The respective methyl esters were saponified and the derived fatty acids were used. Ricinoleic acid was prepared by partition of castor oil mixed fatty acids between light petrol (40-60 C) and aqueous methanol. 12-Hydroxystearic acid was prepared by extraction with light petrol (40-60 C) of non-hydroxy fatty acids from the mixed fatty acids of hydrogenated castor oil. Silica Gel G thin layer chromatography (TLC) showed only traces of non-hydroxy fatty acids in ricinoleic acid, and keto- and non-hydroxy fatty acids in hydroxystearic acid. PEG (600) was obtained from Koch-Light Laboratories, England. Boric acid was reagent grade (The British Drug Houses Ltd., England).

Preparation of PEG Esters

The general procedure for preparing PEG monoester consisted of reacting PEG with boric acid, esterifying the resulting borate with fatty acid using *p*-toluenesulphonic acid (PTS) as catalyst, and selectively hydrolyzing with a minimum amount of water. A typical preparation is described below.

PEG (600) (0.15 mole) and boric acid (0.049 mole) were heated in a flask in an oil bath at 110 C for 2 hr at 5 mm Hg. After cooling the borate to room temperature, 12-hydroxystearic acid (0.14 mole) and PTS (1% on the weight of the reactants) were added and again heated as above for 3 hr. After cooling and neutralizing PTS with sodium acetate, the borate ester was selectively hydrolyzed by heating with water (10 ml) on a steam bath for 1 hr under stirring. To remove free PEG, the product and saturated brine solution (150 ml) were shaken occasionally in a separatory funnel while being kept in an oven (95 C) for 30 min. The aqueous layer was allowed to separate and be withdrawn. The treatment was repeated three times. Silica Gel G TLC of the product using ethyl acetate:acetic acid: water (40:30:30 v/v) as developer and Dragendorff reagent for detection showed the absence of free PEG in the product (9). The product had acid, saponification and iodine values, 3.9, 64.7 (Calc. 63.61), and 1.4, respectively. In different preparations the acid values ranged from 2 to 8 and the yields from 80-85%. The products (100 g) were dissolved in diethyl ether or a mixture of diethyl ether and chloroform and passed through a bed of ground mixture of silica gel (100 g) and sodium hydroxide (5 g) in a sintered funnel, to obtain neutral PEG esters in 71-75% yield. The analytical characteristics of various purified PEG monoesters are reported in Table I.

Surface-Active Properties

Surface-tension measurements were made using a DuNouy tensiometer. Foaming properties were determined using a Ross-Miles pour-foam apparatus (10). Emulsifying power was determined by giving ten downward shakes to a mixture of 40 ml surfactant solution and 40 ml liquid paraffin taken in a 500 ml stoppered conical flask followed by pouring the emulsions in a 100 ml measuring cylinder. The time taken for separation of 10 ml of the aqueous phase was recorded (11). Wetting tests were carried out by the method of Draves-Clarkson as codified by the Indian Standards Institution (12).

RESULTS AND DISCUSSION

In this investigation pure (PEG 600) monoesters of a variety of fatty acids have been prepared to correlate the structural differences in hydrophobic moiety with the surface-active properties. Monoesters are not obtained in good yield by ethoxylation of fatty acids or acid-catalyzed esterification without resorting to a number of purification steps. Esterification of borate of PEG (600), obtained by reaction of boric acid and PEG, with the chosen fatty acid gave monoester in 80-85% yield. Free fatty acids (1-4%) were removed by passage through an alkaline silica gel bed. The analytical constants (Table I) and TLC showed them to be pure.

Surfactant solutions of the pure monoesters were prepared in distilled water. At room temperature, 0.5% aqueous solutions of undecenoate, laurate, myristate, oleate, and ricinoleate were clear while those of palmitate

TABLE I

Characteristics and Surface-Active Properties of PEG[a] (600) Monoesters of Fatty Acids

Monoester	Saponification value		Acid value	Surface tension (dynes/cm at 25 C)			Foaming power (mm) at 30 C				Emulsification at 30 C (time in seconds for separation of 10 ml aqueous phase)		Wetting power at 30 C (seconds)	
							0.2%		0.5%					
	Found	Calcd.		0.05%	0.1%	0.2%	Initial	After 5 min	Initial	After 5 min	0.2%	0.5%	0.2%	0.5%
Undecenoate	71.1	73.2	1.0	35.0	34.0	34.0	15	5	25	8	220	448	10	2
Laurate	70.8	71.7	0.4	33.0	32.0	31.1	50	42	50	40	215	250	15	7
Myristate	71.2	69.3	0.8	35.3	34.8	34.5	43	35	56	44	140	186	34	18
Palmitate	65.0	66.9	0.6	38.5	38.1	37.2	66	54	70	59	123	215	49	44
Stearate	64.2	64.8	0.4	41.5	39.8	38.7	68	64	-	-	132	-	168	-
Oleate	65.3	64.9	0.0	38.3	36.7	35.6	34	22	39	16	163	193	63	32
Ricinoleate	64.0	63.7	0.0	39.4	38.5	38.0	35	21	40	13	218	327	27	15
12-Hydroxystearate	64.2	63.6	0.0	42.5	41.0	41.0	54	30	57	37	228	285	32	17

[a] Polyoxyethyleneglycol.

and hydroxystearate were a little turbid, and that of stearate was slightly more turbid. Hence, 0.05-0.2% solutions of stearate and 0.05-0.5% solutions of others were used. The surface-active properties of the PEG esters are recorded in Table I.

In general, surface-tension values increased with the increase in the molecular weight of hydrophobic moiety. The presence of double bond and hydroxyl group in the hydrophobe decreased the surface tension as exhibited by stearate, oleate, and ricinoleate. Undecenoate did not fit in the general pattern perhaps because of terminal unsaturation. All PEG esters foamed poorly and the unsaturation further reduced foaming as shown by undecenoate and laurate, and oleate and stearate. Undecenoate is the least foaming of the products studied. Hydrophobes having double bond or hydroxyl group contributed towards better emulsifying properties as demonstrated by stearate, oleate, and ricinoleate. In the products of C_{18} series, the presence of a double bond or hydroxyl group markedly increased the wetting power as exemplified by stearate, oleate, ricinoleate, and 12-hydroxystearate. In wetting power, undecenoate topped the PEG esters at the concentration studied. Wrigley et al. (13) made similar observations with ethoxylates of C_{12}-C_{18} saturated, oleic, and hydroxystearic acids. Poor foaming coupled with good emulsifying and wetting properties make PEG (600) monoesters of undecylenic and ricinoleic acids as surfactants of choice in pesticide and cosmetic formulations.

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