

Preparation and surface active properties of oxypropylated α -hydroxyacids, α -hydroxyesters and α -, β -alkane diols.

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RESUMEN

Preparación y propiedades de tensión superficial de α -hidroxiácidos, α -hidroxiésteres y α -, β -alcanodiolos oxipropilados.

Una serie de α -hidroxiácidos $RCH(OH)CO_2H$, α -hidroxiésteres $RCH(OH)CO_2CH_3$ y α -, β -alcanodiolos se sintetizaron y condensaron con 5-20 moles de óxido de propileno para obtener tensioactivos no iónicos. Se examinaron algunas propiedades fisicoquímicas y de biodegradabilidad de estos productos. Los resultados mostraron que las mejores propiedades humectantes se obtuvieron por adición de 15 grupos oxipropileno a α -hidroximiristato de metilo.

El ácido α -hidroximirístico con 20 moles de óxido de propileno dió la espuma más poderosa. Estudios de biodegradación indicaron que tanto el aumento de la longitud de cadena de los grupos alquilo hidrofóbicos como el número de grupos oxipropileno en el aducto disminuyeron la biodegradación.

PALABRAS-CLAVE: Biodegradación — Propiedades fisicoquímicas — Tensioactivo no iónico (preparación).

SUMMARY

Preparation and surface active properties of oxypropylated α -hydroxyacids, α -hydroxyesters and α -, β -alkane diols.

A series of α -hydroxyacids $RCH(OH)CO_2H$, α -hydroxyesters $RCH(OH)CO_2CH_3$ and α -, β -alkane diols was synthesized and condensed with 5-20 moles propylene oxide to obtain nonionic surfactants. Some of the physicochemical properties and the biodegradability of these products were examined. The results showed that the best wetting properties were obtained by the addition of 15 oxypropylene groups to methyl α -hydroxymyristate. The α -hydroxymyristic acid with 20 moles of propylene oxide gave the highest foam. Biodegradation studies indicated that increasing both the chain length of the hydrophobic alkyl chain or the number of oxypropylene groups in the adduct decreased biodegradation.

KEY-WORDS: Biodegradation — Nonionic surfactant (preparation) — Physicochemical properties.

1. INTRODUCTION

The alkali-catalysed reaction of ethylene oxide with long-chain fatty acids are used for the production of commercially important emulsifiers and non-ionic detergents (1) (2). The properties of nonionics can be varied by choice of the hydrophobic moiety and the number of oxyalkylene molecules of the adduct. As a category, they encompass fatty acids, amides, alcohols, amines and phenol ethoxylates (3).

Isomeric hydroxyethyl tertiary amides were found to be excellent soil wetting agents (4). Early work (5) with essentially homogeneous oxyethylated alcohols and acids showed that the best wetting properties were achieved with alcohols and acids containing 8-10

carbon atoms and surfactants with 2-3 ethylene oxide groups.

Propylene oxide, a less hazardous chemical, reacts like ethylene oxide except that a given number of moles confers less hydrophilic characters and can thus be substituted for ethylene oxide. In a recent paper (6) we described the preparation and surface active properties of oxypropylated diol monoesters of fatty acids. In the present work, a novel series of propylene oxide adducts of alpha hydroxy acids, esters and alkane diols was prepared and their surface active properties as well as biodegradability were examined.

2. EXPERIMENTAL

2.1. Preparation of alpha hydroxy fatty acids

Alpha hydroxy myristic, palmitic and stearic acids were prepared by first bromination of the fatty acids with bromine. The bromo acids were just converted to the acetoxy derivatives and then hydrolysed to the α -hydroxy acids. Bromination was carried out as described by Gilman (7).

2.2. Acetoxylation of α -bromo acids

The preparation of α -acetoxy palmitic and was taken as an example: α -bromo palmitic acid 14 g (0.042 moles) and 48 g (0.048 moles) powdered potassium acetate were refluxed in glacial acetic acid for 4 hr. The solvent was distilled off, the residue extracted with chloroform and washed with water. The solvent was removed and the α -acetoxy acid was crystallized (yield 68%) from petroleum ether (60-80 °C).

2.3. Hydrolysis of the α -acetoxy acids

The α -acetoxy acids (5 g) were hydrolysed by heating with 100 ml aqueous KOH (20%) and 75 ml isopropanol at about 160°C. The cooled mixture was acidified and the crude α -hydroxy acids extracted with ether. The extract was washed with water, distilled and the residue was recrystallized from acetone. The crystallized solids, m. p. 82, 87 and 95°C for α -hydroxy-myristic, palmitic and stearic acids were obtained in 63-70% yield.

2.4. Preparation of alkane diols

The methyl esters of the above mentioned hydroxy acids were obtained by esterification of the acids with methanol as described by Dillan (8). The diols were obtained by reduction of the methyl esters with LiAlH_4 followed by saponification and extraction with ether (9). The products had m.p. 73°, 80° and 86°C for α , β tetradecane, α , β hexadecane and α , β octadecane diols, respectively and hydroxyl value 342.1, 342.3 and 342.6.

2.5. Oxypropylation of α -hydroxy acids, esters and alkane diols

The hydroxy acid ester or alkane diol was stirred with 0.5% triethyl amine and heated to 70° under nitrogen. A slight excess over the calculated amount of propylene oxide (PO) necessary to form adducts of 5, 10, 15 and 20 moles PO was used for each test separately. The rate of addition was regulated to maintain the temperature at 70-90 °C. At the disappearance of the reflux of PO, traces of PO were removed in a rotatory evaporator, the flask was

Table I. Surface properties of α -hydroxy fatty acid propenoxyates (a), α -hydroxy methyl ester propenoxyates (b), and 1,2 alkane diols propenoxyates (c)

Type of propenoxyates	n	Surface tension mN/m 0.1%	Interfacial tension mN/m 0.1%	Cloud point °C	Wetting time second	Foam height mm 0.1%	Emulsion stability min
α -Hydroxy myristic acid (a)	5	30	3.5	-	53	43	96
	10	32	4.3	49	30	72	93
	15	33	5.6	62	15	106	89
	20	35	8.5	>100	22	143	86
α -Hydroxy palmitic acid (a)	5	32	4.3	-	62	40	97
	10	32.5	4.6	47	35	73	95
	15	33.5	5.1	60	16	102	90
	20	34.5	6.8	98	20	136	87
α -Hydroxy stearic acid (a)	5	33	3.5	-	72	34	98
	10	34	4.2	47	53	60	96
	15	35	4.7	58	22	93	91
	20	36.5	7.2	94	20	115	90
α -Hydroxy methyl myristate (b)	5	31.0	3.6	-	43	38	91
	10	31.5	4.3	55	30	77	86
	15	32.5	4.7	73	11	123	80
	20	35.0	4.5	>100	21	126	77
α -Hydroxy methyl palmitate (b)	5	33.0	5.9	-	63	36	92
	10	34.0	5.2	54	28	80	86
	15	36.0	6.2	70	20	106	84
	20	38.0	7.5	>100	25	130	78
α -Hydroxy methyl stearate (b)	5	33.0	4.1	-	77	38	94
	10	35.1	4.6	54	52	46	86
	15	36.0	5.9	68	32	102	82
	20	37.1	6.8	97	28	134	80
1,2-Tetradecane diol (c)	5	34.0	3.9	-	76	30	93
	10	35.5	4.1	60	49	42	92
	15	36.5	4.4	82	30	85	90
	20	39.0	5.2	>100	33	102	86
1,2-Hexadecane diol (c)	5	33.0	4.5	-	80	28	94
	10	36.0	4.9	56	62	39	92
	15	36.5	4.6	79	36	65	91
	20	37.5	5.1	>100	40	87	88
1,2-Octadecane diol (c)	5	32.0	4.9	-	81	33	96
	10	34.0	4.6	58	66	42	93
	15	36.0	5.1	76	40	70	90
	20	36.0	7.5	>100	37	81	88

n: average number of propylene oxide moles.

cooled and weighed. Addition of PO was repeated until the weight increase corresponded to the selected PO moles.

The nuclear magnetic resonance (NMR) of the propenoxylated derivatives showed the characteristic spectrum of these types of compounds: CH_3 (0.89 ppm) the paraffinic $(\text{CH}_2)_x$ groups at 1.2-ppm and the protons of oxypropylene units as a broad multiplet at 3.2-3.7 ppm. NMR Spectra were recorded on a Varian EM-390 spectrometer operating at 90 MHz. Deuterated chloroform was used as solvent and tetramethylsilane as internal standard.

2.6. Surface active properties.

Surface tension measurements were made using a Du Noüy tensiometer at $25^\circ\text{C} \pm 0.5$.

Interfacial tension of aqueous solutions (0.1%) of surfactants against heptane (b.p. 208 c) was done in Du Noüy's tensiometer at $25^\circ\text{C} \pm 0.5$. The test solutions were aged at this temperature for at least 1 hr before each measurement of the surface and interfacial tension.

The cloud points were determined by preparing a 1% solution of each material. About 15 ml of each solution in a 30 ml test tube was placed in a water bath that was slowly heated while the solution was stirred with a thermometer. The temperature at the first visual sign of cloudiness or opalescence was recorded. The solution was then removed and allowed to cool slowly while being stirred. The first visual sign of clearing was recorded. Agreement of the two temperatures was generally within 0.5°C .

Wetting ability was determined by the Draves-clarkson method as modified by the Indian Standard Institution (10) using 5.0 g cotton skeins and a 3.0 g hook.

Foaming ability was measured by the Ross and Miles test (11), and the emulsification power was tested as described previously (6).

Biodegradation was evaluated according to Peter et al (12) by surface tension measurements. Biodegradation = $(\gamma_t - \gamma_0) / (\gamma_{bt} - \gamma_0)$ where $\gamma_t = \gamma$ at time t, $\gamma_0 = \gamma$ at time zero (initial) and $\gamma_{bt} = \gamma$ of blank at time t (i.e., without sample).

All results were expressed so that each value was obtained as the average of three determinations.

3. RESULTS AND DISCUSSION

The most important surface active characteristics of the oxypropylene adducts are summarized in Table I.

Comparative aqueous solubility was conveniently expressed by the cloud point. In each series of compounds, solubility increases smoothly as a function of oxypropylene oxide units, as evidenced by an increase in cloud point. However, for the same number of oxypropylene moles, increasing carbon chain length of the hydrophobic alkyl moiety decreases cloud point. Water solubility of the propoxylates is a measure of the ability of the propylene oxide chain to interact via hydrogen bonding with water molecules. When heat is applied to the propoxylate it becomes less soluble due to a reduction in the degree of hydration of the PO chain. In general, the solubility of diol propenoxylates exceeds that of the esters and hydroxy acid homologs, as indicated by higher cloud points.

All derivatives possessed a considerable ability to reduce the surface tension due to their amphipathic molecular structure. Adducts of α -hydroxy acids effected the greatest surface tension lowering (30-35 mN/m). The shorter the length of the hydrophobic alkyl chain the greater the tendency to reduce the surface tension.

Foaming was directly related to the number of propylene oxide groups in the adduct, α -hydroxy myristic acid with 20 PO groups produced the highest foam (143 mm), though these compounds may be considered as moderate or low-foam producers. It is noteworthy that low-foam surfactants are important in some applications such as dyeing auxiliaries in the modern textile industry (13).

The wetting properties varied with the molar propylene oxide levels as well as the structure of the compound. The best overall wetting (11 seconds) occurred by α -hydroxy methyl myristate with 15 oxypropylene groups.

The combined reasonable water solubility, good wetting and relatively low-foaming of this molecular species suggest its possible use as wetting agent in some textile processing performed at relatively high temperature.

Solutions of these compounds lose 70-96% of their surface-active lowering effect within the limits of a 5 days period, suggesting that they are readily biodegradable in

Table II. Biodegradability % of α -hydroxy fatty acid propenoxylates

Type of propenoxylates	n	1st day	2nd day	3rd day	4th day	5th day	6th day
α -Hydroxy myristic acid	5	59	68	79	84	96	-
	10	57	65	74	80	90	-
	15	56	61	72	79	85	93
	20	43	58	68	75	83	90
α -Hydroxy palmitic acid	5	52	67	76	83	93	-
	10	47	63	73	76	86	92
	15	45	59	69	74	83	89
	20	43	54	67	71	79	83
α -Hydroxy stearic acid	5	50	62	70	80	88	90
	10	45	58	68	75	83	87
	15	41	53	66	72	79	83
	20	38	50	62	70	76	79

Table III. Biodegradability % of α -hydroxy methyl ester propenoxyates

Type of propenoxyates	n	1st day	2nd day	3rd day	4th day	5th day	6th day
α -Hydroxy methyl myristate	5	63	68	77	83	92	-
	10	52	65	76	82	91	98
	15	43	57	71	79	88	96
	20	40	49	67	77	86	93
α -Hydroxy methyl palmitate	5	57	64	73	81	89	97
	10	47	59	72	79	86	94
	15	40	55	69	78	81	89
	20	37	48	66	74	79	85
α -Hydroxy methyl stearate	5	53	62	70	79	86	92
	10	45	56	69	72	83	88
	15	37	51	67	70	79	83
	20	35	47	63	69	73	79

Table IV. Biodegradability % of 1,2-alkane diol propenoxyates

Type of propenoxyates	n	1st day	2nd day	3rd day	4th day	5th day	6th day
1,2-Tetradecane diol	5	53	61	74	83	94	-
	10	51	60	67	78	91	-
	15	49	57	62	76	88	96
	20	43	55	60	73	87	94
1,2-Hexadecane diol	5	49	59	70	82	91	-
	10	48	52	63	75	87	97
	15	45	50	62	74	83	93
	20	40	49	57	69	80	91
1,2-Octadecane diol	5	49	55	62	79	87	90
	10	46	51	59	67	78	88
	15	40	48	57	67	72	85
	20	33	42	53	65	70	79

the environment (Table II-IV). The loss of surface activity, taken as an index of biodegradation, was effected by both the chain length of the hydrophobic chain and the number of oxypropylene groups in the adducts. The slower biodegradation of the long-chain adducts may probably be due to the difficulty of the diffusion of the molecule through the cell membrane of the microorganisms (14). Though, the test is one means of characterizing a readily biodegradable compound from one that is more resistant to microbial attack.

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