Benzyl, Cyclohexyl, and Phenyl Esters of *alpha*-Sulfo Fatty Acids[1]

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Abstract

Sodium salts of benzyl, cyclohexyl, and phenyl esters of α-sulfopelargonic, α-sulfopalmitic, and α-sulfostearic acids were prepared by reaction of the α-sulfo acid with excess of the alcohol or phenol, in the presence of methylene chloride, carbon tetrachloride, benzene, or toluene. Synthesis from the acid chloride of the α-sulfo acid gave lower yields of a less pure product.

Melting point, surface and interfacial tension, critical micelle concentration, rate of hydrolysis and wetting, foaming and detergent properties were measured. The ring esters have properties similar to the corresponding propyl, butyl, or amyl esters.

Introduction

A NUMBER OF SODIUM ALKYL α-sulfopelargonates, α-sulfopalmitates, and α-sulfostearates have been prepared, and their surface-active properties have been determined, including esters of primary and secondary alcohols, allyl alcohol, and sodium isethionate (4,5). It was of interest to examine esters of representative ring compounds, namely the esters of benzyl alcohol, cyclohexanol, and phenol.

Two methods of preparation were tried: synthesis by way of the acid chloride and esterification of the α-sulfo acid with an excess of the alcohol or phenol in the presence of an azeotroping agent. The acid chloride method required an extra step and usually gave lower yields because of diester formation (7). Direct esterification with methylene chloride, carbon tetrachloride, benzene, or toluene as the azeotroping agent was successful in each case and was preferred.

Esterification of phenol has usually required the use of an acid chloride or acid anhydride or, with fatty acids, has required the use of a catalyst, high temperatures, and a long reaction time (1). With α-sulfo fatty acids the presence of the sulfonic acid group and the use of an azeotroping agent made possible direct esterification of phenol without catalyst at lower temperature in shorter time.

Experimental Section

Purified pelargonic, palmitic, or stearic acid, suspended or dissolved in carbon tetrachloride, was sulfonated with liquid sulfur trioxide (4). The α-sulfopalmitic and α-sulfostearic acids were isolated as light gray solids. The α-sulfopelargonic acid was first isolated as the monosodium salt, then converted to the free acid by using a Dowex 50WX8 ion exchange column.

Preparation of the esters is illustrated in three cases. Purity was shown by Na analyses (average deviation from theory 0.13%) and ultraviolet and infrared absorption spectra.

Sodium Benzyl α-Sulfopalmitate

A mixture of 0.16 moles of α-sulfopalmitic acid, 0.48 moles of benzyl alcohol, and 500 ml of methylene chloride was refluxed 12 hr at 41C with azeotropic removal of water of esterification. Use of a low boiling solvent prevented the partial decomposition of benzyl alcohol, which takes place at higher temperatures under acid conditions. The mixture was neutralized with sodium hydroxide in aqueous ethanol, crystallized at −25C, recrystallized from absolute ethanol, and again crystallized from hexane containing 10% acetone to give sodium benzyl α-sulfopalmitate, yield 51%. Found 5.18% Na; calculated for $C_{23}H_{37}NaO_5S$, 5.13% Na.

Sodium Cyclohexyl α-Sulfostearate

A mixture of 0.12 moles of α-sulfostearoyl chloride, 0.37 moles of cyclohexanol, and 150 ml of carbon tetrachloride was refluxed 7 hrs, partially neutralized by heating with solid sodium carbonate, cooled, completely neutralized with sodium hydroxide in aqueous ethanol, and filtered. Solid obtained by crystallization from the filtrate at −25C was extracted with toluene to remove cyclohexanol and then recrystallized from ethanol to give sodium cyclohexyl α-sulfostearate, yield 44%. Found 4.94% Na; calculated for $C_{24}H_{45}NaO_5S$, 4.91% Na.

Sodium Phenyl α-Sulfopalmitate

A mixture of 0.15 moles of α-sulfopalmitic acid, 0.46 moles of phenol, and 400 ml of toluene was refluxed 12 hr at 110C with azeotropic removal of water, cooled, and neutralized with sodium hydroxide in aqueous ethanol. After removal of solvent the residue was dissolved in water and extracted with toluene to remove phenol. Ethanol added to the concentrated aqueous solution precipitated disodium α-sulfopalmitate. Crystallization from the clear filtrate at −25C gave sodium phenyl α-sulfopalmitate, yield 40%. Found 5.21% Na; calculated for $C_{22}H_{35}NaO_5S$, 5.29% Na.

Properties are shown in Table I. Melting points were determined with the Fisher-Johns apparatus, surface and interfacial tension with the duNoüy tensiometer, critical micelle concentration (cmc) by dye titration, and biodegradability by the river water die-away test (6). Foam, detergency, wetting and lime soap-dispersing power were measured as in previous publications (5).

The ultraviolet spectra of aqueous solutions of the esters were measured with a Perkin-Elmer Model 202 spectrophotometer. Sodium benzyl α-sulfopalmitate was found to absorb at 4 peaks: 244, 251 (strongest), 258, and 263 mμ ($\epsilon = 1320$, 1770, 1500, 910 respectively). Sodium cyclohexyl α-sulfopalmitate does not absorb in the range 220–390 mμ. Sodium phenyl α-sulfopalmitate was found to absorb like the benzyl ester with peaks at 254 (strong) and 260 ($\epsilon = 365$, 322).

Infrared absorption spectra of carbon tetrachloride solutions of the esters were measured with a Perkin-Elmer Model 137. Sodium benzyl α-sulfostearate showed strong bands close to 3000, 1725, 1475, 1060, 725, and 695 cm^{-1} and a broad band at 1420–1140

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TABLE I

Benzyl, Cyclohexyl, and Phenyl Esters of α-Sulfo Acids

	Melting point °C	cmc mmoles per liter	Surface and interfacial tension 0.1% dynes/cm		Foam and detergency 0.25% built solutions 300 ppm, 60C		Wetting time 0.1% 25C sec	Lime soap-dispersing power %	Biodegradability Time in hours[b]
			S.T.	I.T.	mm	ΔR[a]			
Na Benzyl α-sulfopelargonate	116–118	21.4	53.5	26.4	85[c]	12	56	>100	280
Na Cyclohexyl α-sulfopelargonate	142–143	20.6	48.7	22.1	55[c]	14	83	>100	320
Na Phenyl α-sulfopelargonate	86–88	37.3	53.5	28.0	60[c]	12	>300	>100	320
Na Hexyl α-sulfopelargonate	>200	6.9	26.8	7.1	195	17	2	65	265
Na Benzyl α-sulfopalmitate	121.5–122	0.12	34.3	4.4	180	20	46	15	110
Na Cyclohexyl α-sulfopalmitate	115–117	0.11	35.9	5.5	160	18	29	16	225
Na Phenyl α-sulfopalmitate	93–94	0.20	37.1	7.2	180	20	33	12	250
Na Propyl α-sulfopalmitate	63–65	0.24	37.4	8.4	185	19	16	8	140
Na Amyl α-sulfopalmitate	61–62	0.13	32.9	4.2	140	19	49	....	.....
Na Benzyl α-sulfostearate	100–101	0.07	35.4	4.5	150	18	>300	16	115
Na Cyclohexyl α-sulfostearate	111–112.5	0.06	36.7	2.5	85	19	270	19	130
Na Phenyl α-sulfostearate	78.5–79.5	0.08	37.4	3.1	145	19	115	13	105
Na Propyl α-sulfostearate	72.3–73.6	0.07	37.6	6.9	145	18	70	12	110
Na Amyl α-sulfostearate	65–66	0.07	34.2	4.2	55	19	>300	....	...

[a] Increase in reflectance after washing standard soiled cotton. Value for sodium dodecyl sulfate = 15.

[b] Time in hours for degradation from 5 to 1 ppm (6).

[c] Unstable foam.

cm^{-1}. Sodium cyclohexyl α-sulfostearate: strong bands close to 3025, 1740, 1475, 1060, 1020, and 725 cm^{-1} and a broad band at 1430–1150 cm^{-1}. Sodium phenyl α-sulfostearate: strong bands close to 3025, 1640, 1475, 1375, 1060, 715, and 690 cm^{-1}.

Rate of hydrolysis was measured by heating 0.01 mole of the ester in 100 ml of N/3 H_2SO_4 or N/10 NaOH at 100C and titrating aliquots at selected intervals.

Results and Discussion

The sodium benzyl, cyclohexyl, and phenyl α-sulfopelargonates are more like simple electrolytes than colloidal electrolytes. Values for surface and interfacial tension and cmc are high, and the esters have little or no foaming, wetting, detergent or lime soap-dispersing properties. They resemble shorter-chain esters of α-sulfopelargonic acid rather than the hexyl ester, which is an excellent wetting agent.

TABLE II

Acid and Alkaline Hydrolysis at 100C

Ester of α-sulfopalmitic acid	k_A N/3 H_2SO_4	k_B N/10 NaOH
Benzyl	0.0030	0.13
Cyclohexyl	0.0034	0.0047
Phenyl	0.0041	0.27
Propyl	0.0038	0.032

$$k_A = \frac{1}{t} \ln \frac{a}{a - x} \quad (\mathrm{min}^{-1})$$

$$k_B = \frac{1}{t} \frac{x}{a\,(a - x)} \quad (\mathrm{liters} \cdot \mathrm{moles}^{-1} \cdot \mathrm{min}^{-1})$$

Sodium benzyl, cyclohexyl, and phenyl α-sulfopalmitates and stearates are detergents and lime soap-dispersing agents. They resemble the propyl, butyl, or amyl esters in the properties listed in Table II rather than the corresponding hexyl or heptyl esters. This can be expected since studies on n-alkylbenzenesulfonates have shown the presence of the benzene ring equivalent to 3.5 carbon atoms (2,3). The benzyl, cyclohexyl, and phenyl esters are easily soluble in water, chloroform, ethanol, and toluene but have limited solubility in petroleum ether, ethyl ether, and mineral oil.

Rate of Hydrolysis

There was very little difference in the rate of acid-catalyzed hydrolysis, as shown in Table II.

Hydrolysis in the presence of an equivalent amount of alkali showed the phenyl ester to be the most rapidly hydrolyzed. The benzyl ester was hydrolyzed at the same rate as the methyl ester and the cyclohexyl at about the same rate as the isopropyl ester (4).

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