NOTE

Synthesis and Surface Active Properties of Sodium-3-Alkoxy- and 3-[Alkylmono (di) (oxyethylene) oxy]-2-hydroxy-1-propanesulfonates

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The synthesis and surface active properties of sodium 3-alkoxy- and 3-[alkylmono(di) (oxyethylene)oxy]-2-hydroxy-1-propanesulfonates were investigated. Of all surface active compounds, those with a 2-hydroxypropyl (HP) moiety in the molecules were found more surface-active than the corresponding compounds without it.

1 Introduction

Alkylpoly(oxyethylene) sulfate (AES) is a good anionic surfactant. But AES can be slowly hydrolyzed in aq. solutions, because of the presence of "OSO₃Na" at the terminal of the molecule. As for alkylpoly (oxyethylene) sulfonate the end group of sulfur atom is bound directly to carbon atom. Therefore, it is not readily hydrolyzed. Dahama-yake reported alkoxyethylenesulfonate with one oxyethylene(OE) unit¹⁾. we studied alkyl-di(tri)(oxyethylene) sulfonates with two or three OE unit²⁾. This paper deals with the preparation of sodium 3-alkoxy- and 3-[alkylmono(di)(oxyethylene)oxy]-2-hydroxy-1-propanesulfonates and their surface-active properties.

2 Experimental

2.1 Measurements for surface active properties

The cmc was determined by a surface tension method in quartzcondensed redistilled water using a Shimadzu ST-1 tensometer. The Krafft point (T_{Kp}) was determined by visual observation³⁾. Lime soap dispersing requirement (LSDR) was measured using sodium oleate in hard water⁴⁾. A smaller LSDR value means a stronger lime dispersing power. Calcium ionic stability (ppm Ca-

CO₃) was measured using 1 % Ca(OAc)₂ aqueous solution⁵⁾.

2.2 Synthesis of sodium 3-alkoxy- and 3-[alkylmono(di)(oxyethylene)oxy]-2-hydroxy-1-propanesulfonates

Reaction : $RBr + H(OC_2H_4)_nOH$

(1)

1) 2-[Alkyl(oxyethylene)oxy] ethanols were prepared by Gibson's method⁶⁾: the reaction of RBr with diethylene glycol, about 75 % yield. They were colorless liquid. C₁₂H₂₅(EO)OH : bp 157~160°C/6 mmHg, n_D^{25} 1.4436 (ref. 1.4439). C₁₂H₂₅(EO)₂OH : bp 180~182°C/5 mmHg, n_D^{25} 1.4465 (ref. 1.4465). C₁₄H₂₉(EO)₂OH : bp 200~204°C/5.5 mmHg. C₁₆H₃₃(EO)₂OH : bp 224~226°C/6 mmHg.

2) Alkylmono(di)(oxyethylene) glycidyl ethers were prepared by Urata's method⁷⁾: 2-[alkyl(oxyethylene)oxy]ethanols was reacted with epichlorohydrin in the presence of Bu₄N⁺Br⁻ in *n*-hexane/water solvent at 90 % yield. The crude products obtained proceeded to the following reactions.

3) Sodium 3-alkoxy- and 3-[alkylmono (di)(oxyethylene)oxy]-2-hydroxy- propane-

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Table-1 IR, ^1H -NMR spectra and element analysis of $\text{R}(\text{OC}_2\text{H}_4)_n\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SO}_3\text{Na}$ $0.5 \text{ H}_2\text{O}$.

Compound R	n	IR (cm^{-1})	^1H -NMR (ppm)	Anal. (%) Found (Calcd.)
$\text{C}_{12}\text{H}_{25}$	0	3357 (ν_{OH})	0.92 (3 H, t, CH_3)	C 50.90 (50.74)
		2917, 2833 (ν_{CH})	1.33 [20 H, s, $(\text{CH}_2)_{10}$]	H 9.03 (9.10)
		1200, 1035 ($\nu_{\text{S=O}}$)	3.09 (2 H, d, $\text{CH}_2\text{SO}_3\text{Na}$)	S 9.81 (9.03)
		1167, 1110 ($\nu_{\text{C-O-C}}$)	3.56 (4 H, m, CH_2OCH_2)	
			4.28 (1 H, m, CH)	
$\text{C}_{12}\text{H}_{25}$	1	3311 (ν_{OH})	0.98 (3 H, t, CH_3)	C 51.26 (51.10)
		2900, 2814 (ν_{CH})	1.30 [20 H, s, $(\text{CH}_2)_{10}$]	H 9.04 (9.08)
		1220, 1047 ($\nu_{\text{S=O}}$)	3.06 (2 H, d, $\text{CH}_2\text{SO}_3\text{Na}$)	S 7.88 (8.02)
		1177, 1133 ($\nu_{\text{C-O-C}}$)	3.65 (8 H, m, $\text{CH}_2\text{OC}_2\text{H}_4\text{OCH}_2$)	
			4.25 (1 H, m, CH)	
$\text{C}_{12}\text{H}_{25}$	2	3357 (ν_{OH})	0.90 (3 H, t, CH_3)	C 52.02 (52.50)
		2897 (ν_{CH})	1.32 [20 H, s, $(\text{CH}_2)_{10}$]	H 8.95 (9.06)
		1226, 1047 ($\nu_{\text{S=O}}$)	3.06 (2 H, d, $\text{CH}_2\text{SO}_3\text{Na}$)	S 7.37 (7.38)
		1178, 1130 ($\nu_{\text{C-O-C}}$)	3.70 [12 H, m, $\text{CH}_2(\text{OC}_2\text{H}_4)_2\text{OCH}_2$]	
			4.28 (1 H, m, CH)	
$\text{C}_{14}\text{H}_{29}$	1	3345 (ν_{OH})	0.90 (3 H, t, CH_3)	C 53.60 (53.36)
		2904, 2833 (ν_{CH})	1.31 [24 H, s, $(\text{CH}_2)_{12}$]	H 9.30 (9.45)
		1220, 1035 ($\nu_{\text{S=O}}$)	3.09 (2 H, d, $\text{CH}_2\text{SO}_3\text{Na}$)	S 7.68 (7.50)
		1173, 1130 ($\nu_{\text{C-O-C}}$)	3.66 (8 H, m, $\text{CH}_2\text{OC}_2\text{H}_4\text{OCH}_2$)	
			4.29 (1 H, m, CH)	
$\text{C}_{14}\text{H}_{29}$	2	3367 (ν_{OH})	0.88 (3 H, t, CH_3)	C 53.37 (53.46)
		2892, 2828 (ν_{CH})	1.29 [24 H, s, $(\text{CH}_2)_{12}$]	H 9.20 (9.42)
		1215, 1023 ($\nu_{\text{S=O}}$)	3.04 (2 H, d, $\text{CH}_2\text{SO}_3\text{Na}$)	S 6.83 (6.80)
		1170, 1130 ($\nu_{\text{C-O-C}}$)	3.66 [12 H, m, $\text{CH}_2(\text{OC}_2\text{H}_4)_2\text{OCH}_2$]	
			4.29 (1 H, m, CH)	
$\text{C}_{16}\text{H}_{33}$	1	3357 (ν_{OH})	0.91 (3 H, t, CH_3)	C 55.29 (55.34)
		1928, 2849 (ν_{CH})	1.34 [28 H, s, $(\text{CH}_2)_{14}$]	H 9.47 (9.75)
		1206, 1054 ($\nu_{\text{S=O}}$)	3.09 (2 H, d, $\text{CH}_2\text{SO}_3\text{Na}$)	S 7.08 (7.03)
		1180, 1134 ($\nu_{\text{C-O-C}}$)	3.67 (8 H, m, $\text{CH}_2\text{OC}_2\text{H}_4\text{OCH}_2$)	
			4.28 (1 H, m, CH)	
$\text{C}_{16}\text{H}_{33}$	2	3357 (ν_{OH})	0.89 (3 H, t, CH_3)	C 55.30 (55.27)
		2904, 2833 (ν_{CH})	1.31 [28 H, s, $(\text{CH}_2)_{14}$]	H 9.55 (9.70)
		1217, 1029 ($\nu_{\text{S=O}}$)	3.09 (2 H, d, $\text{CH}_2\text{SO}_3\text{Na}$)	S 6.78 (6.42)
		1172, 1130 ($\nu_{\text{C-O-C}}$)	3.67 [12 h, m, $\text{CH}_2(\text{OC}_2\text{H}_4)_2\text{OCH}_2$]	
			4.31 (1 H, m, CH)	

sulfonates (1) were synthesized as following :

In a 500 mL stainless steel autoclave were put a mixture of water (100 mL), acetone (33 mL), sodium metabisulfite (7.3 g), sodium sulfite (6.1 g) and crude products of alkylmono(di)(oxyethylene) glycidyl ethers

(0.1 mol). The mixture was stirred vigorously and heated rapidly to $120\sim 140^\circ\text{C}$ for 4 h at $500\sim 989$ Pa pressure. The reaction mixture was cooled to 50°C and was taken out. After the acetone and water were distilled out from the reaction mixture, the residue was extracted with 100 mL 2-propa-

Table-2 Comparison of surface activities for $R(OC_2H_4)_nSO_3Na$ and $R(OC_2H_4)_nO[CH_2CH(OH)CH_2]_mSO_3Na$ derivatives.

Surfactant R	n	m	cmc (mM) (25°C)	K. P. (°C) (1 % aq.)	LSDR (%)	Calcium ionic stability (ppm $CaCO_3$)
$C_{12}H_{25}$	1	0	3.60 ^a	28	16	350
$C_{12}H_{25}$	0	1	3.40 ^a	39	7.6	>1,800
$C_{12}H_{25}$	2	0	2.80	<0	5.0	>1,800
$C_{12}H_{25}$	1	1	1.60	4	2.9	>1,800
$C_{12}H_{25}$	3	0	2.30	<0	4.0	>1,800
$C_{12}H_{25}$	2	1	1.40	<0	2.5	>1,800
$C_{14}H_{29}$	3	0	0.32	<0	4.0	>1,800
$C_{14}H_{29}$	1	1	0.16	17	3.4	>1,800
$C_{14}H_{29}$	2	1	0.14	<0	2.9	>1,800
$C_{16}H_{33}$	3	0	0.05	4	4.0	>1,800
$C_{16}H_{33}$	1	1	0.07	22	5.8	>1,800
$C_{16}H_{33}$	2	1	0.06	7	3.4	>1,800

(a). The cmc was measured at 40°C.

nol at boiling temp. and at the same time the organic layer was separated. The organic layer was cooled to 0~5°C and the crystalline product was separated, then it was washed with 20 mL of 2-propanol and 20 mL of petroleum ether. Finally all the products were recrystallized from 100 mL of 2-propanol and the crystalline products were dried *in vacuo* to give the white crystalline (1) at 90 % yield. Their purity were determined with silica gel G plate chromatography, ethanol as a development agent to give pure samples. Elemental analysis, IR and 1H -NMR spectra and listed in Table-1.

3 Results and Discussion

Surface activity of synthetic products with a HP moiety and the corresponding compounds without HP are summarized in Table-2.

All surface-activities such as T_{Kp} , cmc, LSDR and calcium ionic stability for the compounds containing a 2-hydroxypropyl

moiety in the molecule are higher than the corresponding compounds without it. Both EO and HP derivatives excellent hard water-resisting surface activity.

The introduction of HP moiety instead of EO enhances hydrophobic properties, so the cmc becomes smaller.

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