LETTER

Surface Active Properties of New Types of Amphipathic Compounds with Two Hydrophilic Ionic Groups and Two Lipophilic Alkyl Chains

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Disodium 1,8-bis (alkyloxymethyl) -3,6-dioxaoctane-1,8-disulfates and disodium 5,12-bis (alkyloxymethyl) -4,7,10,13-tetraoxahexadecane-1,16-disulfonates (alkyl; octyl or decyl) were prepared from 1,8-bis (alkyloxymethyl) -3,6-dioxaoctane-1,8-diols obtained by reactions of ethylene glycol diglycidyl ether with octyl or decyl alcohol. These new types of compounds showed excellent surface active properties in water.

Amphipathic compounds with plural lipophilic alkyl groups have been widely studied on their applications to the artificial bilayer membrane system¹⁾. There are also some reports on the surface active properties of compounds containing plural lipophilic alkyl groups²⁾ or plural hydrophilic functional groups³⁾.

Recently, we have developed the facile synthetic method of oligo (ethylene glycol) diglycidyl ethers⁴⁾ and studied on the preparation and properties of many functional products from them^{5)~8)}.

In this report we describe the syntheses and the interesting surface active properties of new types of amphipathic compounds (2, 3) which are derived from ethylene glycol diglycidyl ether (EGDG) and have two hydrophilic ionic groups and two lipophilic alkyl chains.

Synthetic routes to 2 and 3 are shown in Fig.-1. Diols (1a, b) were prepared and isolated (ca. 50 % yield) by the reported reaction⁶⁾ of EGDG⁴⁾ with octyl or decyl alcohol. A dichloro-

methane solution of 1 was added to the mixture of chlorosulfonic acid and glacial acetic acid⁹⁾ at 0°C [$\text{ClSO}_3\text{H} : \text{AcOH} : 1 = 10 : 10 : 3$ (molar ratio)]. After 3 h of stirring at room temperature, the reaction mixture was neutralized with 2 N aq Na_2CO_3 and diluted with saturated aq NaHCO_3 . This solution was extracted with *n*-BuOH several times and the evaporation of the solvent gave TLC-pure disodium disulfates (2) [Yield : 2a (viscous liquid); 90 %, 2b (mp : 75~82°C); 87 %]. Disodium disulfonates (3) were prepared by the reaction of propanesultone with 1 in the presence of powdered NaOH at 130°C [$1 : \text{NaOH} : \text{propanesultone} = 3 : 10 : 9$ (molar ratio)]. TLC-pure products were obtained by the *n*-BuOH extraction of the reaction mixture diluted with saturated aq NaHCO_3 and the subsequent evaporation of the solvent [Yield : 3a (mp; 155~170°C); 25 %, 3b (mp; 140~155°C); 30 %]. Their structures were confirmed by ¹H NMR and elemental analyses.

Fig.-1 Synthetic routes to amphipathic compounds (2, 3) with two hydrophilic ionic groups and two lipophilic alkyl chains.

Table-1 Surface active properties of 2, 3, and typical anionics.

Surfactant	T_{KP} (°C)	10^4 cmc (M)	γ_{cmc} (mN·m ⁻¹)	Foam volume (mL)	
				0'	60'
2 a	< 0	6.0	29.2	220	0
2 b	< 0	0.13	27.0	250	100
3 a	< 0	7.0	29.2	140	0
3 b	< 0	0.47	29.0	260	40
C ₁₂ H ₂₅ SO ₃ Na ^{a)}	16	82 ^{b)}	38.5 ^{b)}	--- c)	
C ₁₈ H ₃₇ SO ₃ Na ^{a)}	56	2.3 ^{d)}	40.6 ^{e)}	--- c)	
C ₁₂ H ₂₅ SO ₃ Na ^{a)}	38	97 ^{f)}	37.6 ^{f)}	--- c)	

a) Ref. 11. b) At 25°C. c) Unavailable. d) At 50°C. e) Ref. 12; 0.1% turbid dispersion at 25°C.

f) At 40°C.

The Krafft point (T_{KP}) of 2 and 3 was determined with a 1 wt% aqueous solution. The cmc and the lowering ability of surface tension (γ_{cmc}) were measured by the Wilhelmy method in water at 20°C, and the foaming properties were evaluated by the semi-micro TK method¹⁰⁾ with a 1 wt% aqueous solution of surfactants at 20°C. Surface active properties of these compounds are listed in **Table-1** with reported data of some typical alkyl sulfates and sulfonate^{11), 12)}. Purity of samples was also ascertained from the observed sharp break in each surface tension-logarithm concentration curve.

Since the T_{KP} values of 2 and 3 not only with two octyl groups but also with two decyl groups as the lipophilic part are below 0°C, these compounds in this work possess good water-solubility. It was reported that branched alkyl sulfates²⁾, sulfates with oligo(oxyethylene) group between alkyl chain and terminal sulfate groups¹²⁾, and alkyl- α , ω -disulfates³⁾ showed lower T_{KP} values than linear alkyl sulfates with the same number of carbon atoms in the alkyl group. Although compounds (2, 3) are new types of surfactants, a remarkable decrease of T_{KP} of 2 and 3 may be attributed to the co-operated effect of centrally located hydrophilic part as discussed about branched alkyl anionics²⁾, oxyethylene group, and two sulfate groups. Whereas the cmc value generally increases as the hydrophilicity of the molecule increases in a series of typical anionics¹¹⁾, the cmc values of 2 and 3 and fairly

small in spite of their good hydrophilicity.

Surfactants with plural lipophilic groups generally show lower γ_{cmc} values than ones with a single lipophilic group¹³⁾. The lowering ability of surface tension of 2 and 3 is exceptionally good compared with other anionic surfactants. Moreover the foaming ability of these compounds is also good, and the foam stability of 2 b and 3 b with longer alkyl chains is excellent.

To clarify the correlation between the structure and the properties of these types of compounds, an investigation of the effect of connective group between two lipophilic groups or the kind of both lipophilic and hydrophilic groups on surface active properties is now in progress.

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二つの親水性イオン基と二本の親油性アルキル鎖を有する新しい型の両親媒性化合物の界面活性能

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エチレングリコールジグリシジルエーテルとオクチルアルコールまたはデシルアルコールの反応により得られる1,8-ビス(アルキルオキシメチル)-3,6-ジオキサオクタン-1,8-ジオールを出発物質として, 1,8-ビス(アルキルオキシメチル)-3,6-ジオキサオクタン-1,8-ジ(硫酸ナトリウム)及び5,12-ビス(アルキルオキシメチル)-4,7,10,13-テトラオキサヘキサデカン-1,16-ジ(スルホン酸ナトリウム)を合成した。これらの新しい型の化合物は, 水中で優れた界面活性能を示した。