

SURFACTANTS & DETERGENTS

Preparation and Surface-Active Properties of New Amphipathic Compounds with Two Phosphate Groups and Two Long-Chain Alkyl Groups

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New compounds bearing two dihydrogen phosphate groups and two long-chain alkyl groups (octyl or decyl) were prepared in good yields by the reaction of 1,ω-bis(alkyloxymethyl)-oligo(ethylene glycol)s with polyphosphoric acid.

Amphipathic di- or tetrasodium phosphates were obtained by neutralization of the free acids with sodium hydroxide, and their surface-active properties in water were measured. Almost all these di- or tetrasodium phosphates showed good water solubility. Their abilities to form micelles and to lower surface tension were fairly good as compared with general monoalkyl phosphates consisting of one longer alkyl chain and one hydrophilic group. The foaming property of aqueous solutions of the tetrasodium salts was different from that of the disodium salts. The former showed very low foaming ability.

KEY WORDS: Bis(monoalkyl phosphate) compounds, diepoxy compounds, di- or tetrasodium 1, ω-bis(alkyloxymethyl)-1, ω-diphosphates, low foaming properties, oligo(ethylene glycol) diglycidyl ethers, surfactants with two lipophilic alkyl chains and two ionic head groups.

Surface-active alkyl phosphates are widely used in many industrial or household and personal products, such as antistatic agents for textiles, mold lubricants, detergents, shampoos, emulsifiers, extracting agents for metal ions, and anticorrosives (1-4). Because phospholipids are one of the major components of bilayer cell membranes, the interfacial properties of amphipathic phosphates are of particular interest to chemists concerning liposomes or functional vesicles (5).

Recently, some methods for preparing selectively monoalkyl phosphates have been reported (6-11). It has been found that monoalkyl phosphates have excellent surface-active properties and that they show a lower irritating property for the skin as compared with di- or trialkyl phosphates and various other anionic surfactants (7,8).

We previously developed new types of amphipathic compounds with two octyl or two decyl groups and two sulfate or two sulfonate groups derived from various glycol diglycidyl ethers (12,13). These compounds show good water solubility and are superior in surface-active properties to general anionic surfactants with one lipophilic chain and one hydrophilic group such as sodium dodecylsulfate. We now report that new types of bis(monoalkyl phosphate) compounds (III-V) bearing two lipophilic chains have been prepared in good yields by the reaction of the corresponding 1,ω-(alkyloxymethyl) oligo(ethylene glycol)s (II) with polyphosphoric acid (Fig. 1). In this paper, we present the preparation methods for a

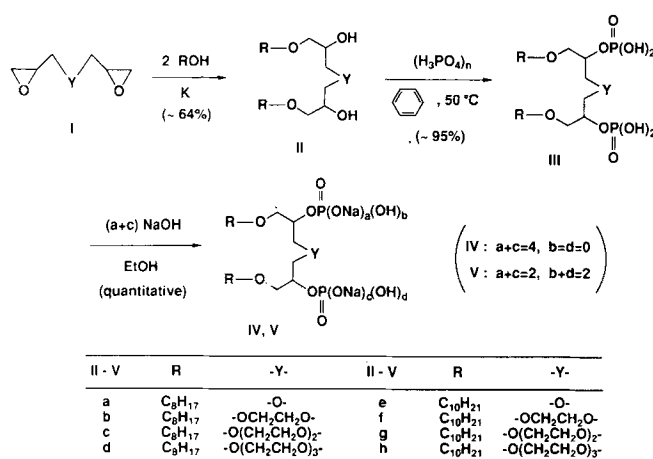


FIG. 1. New types of bis(monoalkyl phosphate) compounds prepared in this work.

series of dihydrogen phosphates (III) and basic surface-active properties of both the tetrasodium salts (IV) and the disodium salts (V) of bis(monoalkyl phosphate) compounds.

EXPERIMENTAL PROCEDURES

Materials. Diepoxy compounds (I) [Di-2,3-epoxypropyl ether, ethylene glycol-, di(ethylene glycol)-, and tri(ethylene glycol) diglycidyl ethers] were prepared under phase-transfer catalytic conditions previously reported by us (14,15). Preparation of 1,ω-bis(alkyloxymethyl)-oligo(ethylene glycol)s (IIa-h) was carried out according to the method described in a previous paper (16). 1,ω-Bis(alkyloxymethyl)-1,ω-bis(dihydrogen phosphate)s (IIIa-h) were synthesized by phosphorylation of the corresponding diols (IIa-h) with polyphosphoric acid in dry benzene at about 50°C. Purification of IIIa-h was performed by solvent extraction and silica gel column chromatography. Their purity and established structure were ascertained by thin-layer chromatography (TLC), high-performance liquid chromatography (HPLC) (ODS column, methanol eluent), spectral (infrared—IR, nuclear magnetic resonance—¹H-NMR, ³¹P-NMR, mass spectra—MASS), and elemental analyses. ³¹P-NMR spectra were recorded on a JEOL JNM-GSX400 spectrometer at 161.8 MHz. 85% D₃PO₄ in D₂O was used as an external standard. Di- and tetrasodium salts (V and IV, respectively) of these phosphates were prepared almost quantitatively by neutralization with two-fold and four-fold molar amount of sodium hydroxide in ethanol, respectively. Their purity was also confirmed from the observed

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TABLE 1

Characterization of 1, ω -Bis(alkyloxymethyl)-1, ω -bis(dihydrogen phosphate)s (IIIa-h)^a

Compound	Yield ^b (%)	¹ H-NMR ^c (δ ,ppm)	Anal. ^d Found (calcd.)
IIIa	73	0.88(<i>t</i> ,6H), 1.10–1.80(<i>m</i> ,24H), 3.30–4.15(<i>m</i> ,12H), 4.60(<i>m</i> ,2H), 8.0–9.0(<i>br</i> ,4H,—OH)	H, 8.51 (8.80) C, 46.18 (46.48)
IIIb	84	0.88(<i>t</i> ,6H), 1.10–1.80(<i>m</i> ,24H), 3.30–4.10(<i>m</i> ,16H), 4.60(<i>m</i> ,2H), 8.0–9.0(<i>br</i> ,4H,—OH)	H, 8.80 (8.68) C, 46.78 (46.91)
IIIc	95	0.88(<i>t</i> ,6H), 1.10–1.80(<i>m</i> ,24H), 3.30–4.10(<i>m</i> ,20H), 4.60(<i>m</i> ,2H), 7.5–8.5(<i>br</i> ,4H,—OH)	H, 8.58 (8.84) C, 47.87 (47.56)
III d	64	0.88(<i>t</i> ,6H), 1.10–1.80(<i>m</i> ,24H), 3.30–4.40(<i>m</i> ,24H), 4.60(<i>m</i> ,2H), 8.0–9.0(<i>br</i> ,4H,—OH)	H, 8.85 (8.85) C, 46.98 (47.94)
IIIe	89	0.88(<i>t</i> ,6H), 1.10–1.80(<i>m</i> ,32H), 3.30–4.40(<i>m</i> ,12H), 4.60(<i>m</i> ,2H), 8.0–9.0(<i>br</i> ,4H,—OH)	H, 8.80 (8.68) C, 46.78 (46.91)
III f	88	0.88(<i>t</i> ,6H), 1.10–1.80(<i>m</i> ,32H), 3.30–4.40(<i>m</i> ,16H), 4.60(<i>m</i> ,2H), 8.0–9.0(<i>br</i> ,4H,—OH)	H, 8.84 (9.28) C, 49.24 (50.29)
IIIg	89	0.88(<i>t</i> ,6H), 1.10–1.80(<i>m</i> ,32H), 3.30–4.10(<i>m</i> ,20H), 4.60(<i>m</i> ,2H), 7.5–8.5(<i>br</i> ,4H,—OH)	H, 9.03 (9.24) C, 49.48 (50.42)
IIIh	85	0.88(<i>t</i> ,6H), 1.10–2.0(<i>m</i> ,32H), 3.30–4.40(<i>m</i> ,24H), 4.60(<i>m</i> ,2H), 8.0–9.0(<i>br</i> ,4H,—OH)	H, 9.56 (9.26) C, 50.02 (50.73)

^a All compounds showed similar IR Spectra (Hitachi 260 spectrometer): 3500, 2980, 2300, 1200, 1100 and 1000 cm⁻¹ (neat). They also showed only one peak at about 0 ppm in their ³¹P-NMR (JEOL JNM-GSX400 at 161.8 MHz, external standard: 85% D₃PO₄). (M⁺+1) peaks of all compounds were observed in their FABMS spectra (JEOL JMS-DX303).

^b Based on diols (II).

^c JEOL JNM-GSX400, 400MHz, s: singlet, t: triplet, m: multiplet.

^d Calculation values are based on the assumption that all compounds contain one molar bonding water.

sharp break point in the surface tension - concentration curves.

1, ω -Bis(alkyloxymethyl)-1, ω -bis(dihydrogen phosphate)s (III): *typical procedure*. A mixture of 1,11-bis(octyloxymethyl)-3,6,9-trioxa-1,11-undecanediol (IIc; 1.43 g, 3 mmol) and dry benzene (15 mL) was dropped into 30 mL of dry benzene solution containing 3.04 g of polyphosphoric acid (117% H₃PO₄ content, 9 mmol) at 50°C. After 72 hr of stirring at 50°C, 20 mL of water was added and the reaction mixture was stirred for 3 hr at 50°C in order to deactivate any excess of polyphosphoric acid. This aqueous solution was extracted with ether (100 mL), and the ether layer was washed with water (60 mL), 2 N hydrochloric acid (50 mL), and water again (2 × 60 mL). The ether solution was then treated with 5% aqueous sodium hydroxide (3 × 60 mL). After the combined aqueous solution was acidified with concentrated hydrochloric acid to pH 1, the resultant solution was extracted with ether (200 mL) again. After evaporation and subsequent washing of the residue with hexane several times, 1.82 g of TLC and HPLC pure 1,11-bis(octyloxymethyl)-3,6,9-trioxaundecane-1,11-bis(dihydrogen phosphate) (IIIc) was isolated as a viscous liquid (95% yield). If the

existence of contaminants, mainly oligophosphoric acid, in final product, was observed by TLC, HPLC, or ³¹P-NMR spectrum, additional purification was done by silica gel column chromatography with a chloroform-ethanol (or methanol) eluent. The preparation results of IIIa-h are listed in Table 1.

Tetrasodium 1, ω -bis(alkyloxymethyl)-1, ω -diphosphates (IV): typical procedure. The tetrasodium salt (IVc) was prepared by neutralizing the corresponding bis(dihydrogen phosphate) (IIIc; 0.60g, 0.94 mmol) with a 20 mL ethanol solution of sodium hydroxide (95%) (0.16 g, 3.76 mmol). After evaporation of the mixture, 0.69 g IVc was obtained as a hygroscopic solid.

Disodium 1, ω -bis(alkyloxymethyl)-1, ω -diphosphates (V): typical procedure. The disodium salt (Vc) was prepared by the reaction of the corresponding phosphate (IIIc; 0.383 g, 0.6 mmol) with a 15 mL ethanol solution of sodium hydroxide (0.05 g, 1.2 mmol). After evaporation of the mixture, 0.43 g of Vc was obtained as a hygroscopic solid.

Methods. The Krafft point (T_{KP}) was determined by the naked eye with a 1 wt% aqueous solution. The surface tension of IV and V was measured with a Wilhelmy

tensiometer using a series of aqueous solutions at various concentrations at 20°C. The foaming properties were evaluated by the semi-micro TK method (17) with a 0.1 wt% aqueous solution of surfactants at 20°C.

RESULTS AND DISCUSSION

Several phosphorylating agents toward alcohols such as phosphorus pentoxide (10,18), phosphorus oxychloride (6,7), pyrophosphoric acid (6,11), phosphorus trichloride (6) and polyphosphoric acid (19) were reported. Among them, employment of phosphorus pentoxide, phosphorus oxychloride and polyphosphoric acid to phosphorylate 1, ω -bis(alkyloxymethyl)-oligo(ethylene glycol)s (II) was tried in this study. When the glycols (II) were treated with phosphorus pentoxide at 50°C, undesirable dehydration of the glycols partially occurred. In the case of phosphorus oxychloride, the reaction mixture was too complex to isolate the target bis(monoalkyl phosphate). In contrast to these reagents, polyphosphoric acid afforded good results. Though some minor by-products were also detected by TLC (three spots) and ^{31}P -NMR in the reaction mixture, the target compounds III could be isolated in good yields by devising the extraction procedure as described in the Experimental Procedures section. All isolated compounds, III, showed only one peak at about 0 ppm in their ^{31}P -NMR spectra. Also, no peak was observed in their ^{31}P -NMR spectra in the regions of δ -10 to δ -15 and δ -30 to δ -40 which were attributed to pyrophosphoric acid (20,21). These results indicated that the isolated products are free from pyrophosphoric acid, which is one of the possible contaminants. The absence of bis(dialkyl phosphate) or bis(trialkyl phosphate) types of compounds in the isolated products was confirmed by their ^1H -NMR, ^{31}P -NMR, and FABMS (Fast Atom Bombardment Mass Spectrometry) spectra.

All these tetrasodium salts (IV) and disodium salts (V) except Va and Ve in this study were readily soluble in water forming a clear solution and the Krafft point of all these compounds was below 0°C. It was reported that monosodium monoalkylphosphates with one lipophilic chain have a lower solubility in water than the corresponding disodium salts (7). Since Va and Ve in this study have only one ether oxygen atom in the connecting group, it is considered that their water solubility is low when compared with the corresponding tetrasodium salts, and therefore they are insoluble. It is surmised that the excellent hydrophilicity of IV and the other, V, may be ascribed to the same reasons as previously described in the paper about amphipathic compounds with two sulfate groups and two lipophilic alkyl chains (13). The plots of surface tension vs concentration for aqueous solutions of IVa-h and Vb-d,f-h are shown in Figures 2 and 3, respectively.

The critical micellar concentration (CMC, determined from the break point of each curve in Figs. 2 and 3) and the ability of these compounds to lower surface tension above the CMC (γ_{CMC}) are listed in Table 2 along with the data for the reference compounds, disodium- and monosodium alkyl phosphates (7).

The CMC values of compounds IV and V were fairly small compared with those of the reference compounds with one dodecyl group. Disodium salts (V) showed lower CMC values than the corresponding tetrasodium salts

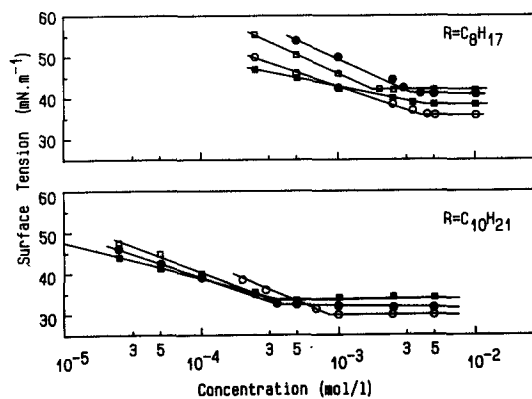


FIG. 2. Surface tension-concentration plots of compounds (IV) in water at 20°C. Y: \circ , $-\text{O}-$; \bullet , $-\text{OCH}_2\text{CH}_2\text{O}-$; \square , $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_2-$; \blacksquare , $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_3-$.

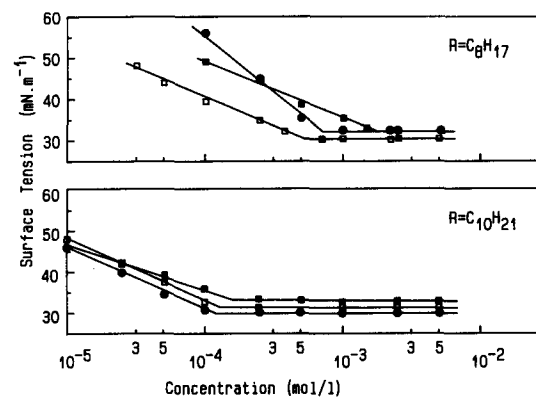


FIG. 3. Surface tension-concentration plots of compounds (V) in water at 20°C by Wilhelmy method. Y: \bullet , $-\text{OCH}_2\text{CH}_2\text{O}-$; \square , $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_2-$; \blacksquare , $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_3-$.

TABLE 2

The CMC and γ_{CMC} Values of Compounds (IVa-h, Vb-d,f-h) and Reference Compounds (20°C)

Compound	R	- Y -	CMC (mM)	γ_{CMC} (mN/m)
IVa	C ₈ H ₁₇	-O-	4.0	36.0
IVb	C ₈ H ₁₇	-OCH ₂ CH ₂ O-	3.3	41.0
IVc	C ₈ H ₁₇	-O(CH ₂ CH ₂ O) ₂ -	1.8	42.0
IVd	C ₈ H ₁₇	-O(CH ₂ CH ₂ O) ₃ -	4.3	38.5
IVe	C ₁₀ H ₂₁	-O-	0.85	30.0
IVf	C ₁₀ H ₂₁	-OCH ₂ CH ₂ O-	0.36	32.5
IVg	C ₁₀ H ₂₁	-O(CH ₂ CH ₂ O) ₂ -	0.31	33.5
IVh	C ₁₀ H ₂₁	-O(CH ₂ CH ₂ O) ₃ -	0.36	33.5
Vb	C ₈ H ₁₇	-OCH ₂ CH ₂ O-	0.72	32.0
Vc	C ₈ H ₁₇	-O(CH ₂ CH ₂ O) ₂ -	0.52	30.5
Vd	C ₈ H ₁₇	-O(CH ₂ CH ₂ O) ₃ -	1.8	32.0
Vf	C ₁₀ H ₂₁	-OCH ₂ CH ₂ O-	0.12	30.0
Vg	C ₁₀ H ₂₁	-O(CH ₂ CH ₂ O) ₂ -	0.13	31.5
Vh	C ₁₀ H ₂₁	-O(CH ₂ CH ₂ O) ₃ -	0.16	33.0
C ₁₂ H ₂₅ OP(O)(ONa) ₂ ^a			40.0	39.5
C ₁₂ H ₂₅ OP(O)(OH)(ONa) ^a			3.5	27.5

^aReference 7.

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TABLE 3

Foaming Properties of Compounds (IVf-h, Vf-h)^a (20°C)

Compound (R = C ₁₀ H ₂₁)	-Y-	Foam volume (mL)	
		0 min	5 min
IVf	-OCH ₂ CH ₂ O-	<10	0
IVg	-O(CH ₂ CH ₂ O) ₂ -	<10	0
IVh	-O(CH ₂ CH ₂ O) ₃ -	<10	0
Vf	-OCH ₂ CH ₂ O-	240	230
Vg	-O(CH ₂ CH ₂ O) ₂ -	230	200
Vh	-O(CH ₂ CH ₂ O) ₃ -	170	0

^a0.1 wt% aqueous solution.

(IV). This result is the same as that found for mono- and disodium monoalkylphosphates. Compounds with a di(oxyethylene) connecting group (IVc,g and Vc,g) showed lower CMC values than compounds with other connecting groups. The effect of the number of oxyethylene units adjacent to an ionic head group on the CMC was previously investigated for sodium alkyl polyoxyethylated sulfates (22). It was clarified that when up to three or four oxyethylene units were in contact with a sulfate group the oxyethylene units appeared to act as a hydrophobic group which contributed to lowering CMC values. A similar effect of the oxyethylene units in the connecting group on the CMC values was also observed in this work.

There was not a remarkable difference in γ_{CMC} values between compounds IVe-h and Vf-h having two decyl chains. The relatively low ability to lower surface tension of tetrasodium salts (IVa-d) having two octyl chains may be attributed to their low lipophilicity. Among the compounds in this work, compound IVe exhibited the maximum ability to lower surface tension. The γ_{CMC} values slightly increased with an increase in the length of the connecting group. When the connecting group is short and/or small, closely packed surface film at the surface will be readily formed. When the connecting group is long and/or bulky, the Van der Waals interaction of alkyl chains between adsorbed molecules at the surface will become weak. This results in a loosely packed surface film on the surface. Similar γ_{CMC} results for compounds Vb-d,f-h were observed to those for compounds IVa-h.

As shown in Table 3, foaming ability and foam stability of tetrasodium salts (IVf-h) contrast with those of the disodium salts (Vf-h). Compounds IVf-h showed both low foaming ability and low foam stability. On the other hand, Vf-h had good foaming abilities. Especially, Vf and Vg with an oxyethylene and di(oxyethylene) connecting group, respectively, showed excellent foaming ability and foam stability. In the case of the tetrasodium salts (IVf-h), four anionic heads in the hydrophilic moiety will

increase the electrostatic repulsion between the surfactant molecules adsorbed onto the foam. This results in low foaming ability and low foam stability of IVf-h.

New amphipathic compounds with two phosphate groups and two long-chain alkyl groups studied in this work possessed good water solubility, micelle forming properties, and the ability to lower surface tension in comparison with general phosphate types of surfactants consisting of one lipophilic group and one hydrophilic functional group. It was also found that their foaming properties strongly depended on the number of sodium atoms in the molecules.

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