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# Preparation and characterization of hydrophobically modified alginate

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## Summary

Biodegradable alginate-derived polymeric surfactants (APSs) with a linear alkyl group (C8, C12, C16) were synthesized by oxidation followed by reductive amination of 2,3-dialdehydic alginate. The oxidized alginates and all APSs were characterized by spectral and X-ray diffractometry analysis. The sonicated suspension test was employed to form self-aggregates in aqueous solution. In the case of 40% CHO-C8 APS, the lowest interfacial tension, 31.5 $mNm^{-1}$, was obtained at the c.m.c. value of 1.35 g $L^{-1}$. A biodegradability test on the 30% CHO-C12 APS system suggested that it would be attacked by a soil microorganism, *Aspergillus niger*.

## Introduction

Among the industrially attractive biopolymers, alginate is known to have high complexing ability with various heavy metal ions and used as adsorbents for the recovery of valuable metals or the removal for the toxic metals [1,2]. It contains 1,4-linked β-D-mannuronic (M) and α-L-guluronic (G) acid residues arranged in a nonregular, blockwise fashion along the chain (Figure 1). Generally G-blocks are responsible for the "egg box" formation with calcium ions during alginate gelation [3,4], whereas MG-heteroblock frequency governs the solubility of alginic acid at low pH [5]. However, two types of derivatives were reported due to the low reactivity of hydroxyl groups in alginate [6]. The one is alginate esters, and the other is a crosslinkable alginate. Among these derivatives, the only derivative having a commercial value is the propylene glycol esters of alginate (PGA) that is obtained by an esterification of alginate with propyleneoxide. Until now studies on alginate-derived surfactants were not performed sufficiently in spite of its merit of metal removal and water solubility.

In soil washing or flushing technique, chelating agents and surfactants were generally used as the extracting additives. There has been an increasing interest in using biodegradable surfactant solutions recently, because these agents have low toxicity to humans, animals and plants [7]. More research is required to develop the environmentally friendly soil washing agents. Here the sodium alginate chosen as a naturally occurring polymer was used to make a new 'biopolymer surfactant'.

The newly synthesized alginate-derived polymeric surfactants (henceforth referred to

as APSs) have not only carboxyl groups of original alginate, but also long-chain alkyl amines. From the practical point of view, it could be applicable to the removal of heavy metals and organic compounds from soil contaminated with mixed wastes. The objectives of the present paper are the preparation of biodegradable surface-active agents derived from alginate and characterized by surface activity, self-aggregates formation, and biodegradability test.

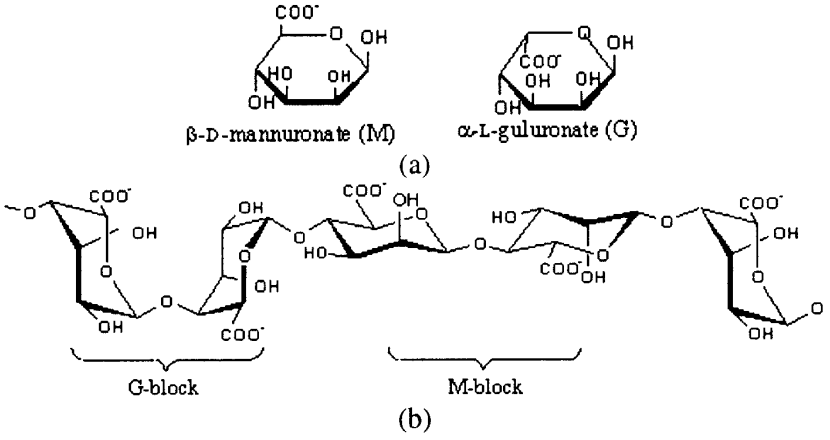



**Figure 1.** Chemical structures of (a) alginate monomers and (b) conformational chain of alginate

## Experimental

### *Materials*

Alginic acid sodium salt (low viscosity, derived from *Macrocystis pyrifera*) was purchased from Sigma (USA). Sodium periodate, sodium cyanoborohydride, octyl amine ($C_8H_{17}$-$NH_2$), dodecyl amine ($C_{12}H_{25}$-$NH_2$), and hexadecyl amine ($C_{16}H_{33}$-$NH_2$) were obtained from Aldrich Chemical Co. and used as received. 1-Propanol, ethanol (95%) and ethylene glycol were from Junsei Co. (Japan).

### *Instruments*

Transmission IR spectra of alginate and APSs were recorded on a FTIR spectrophotometer (JASCO FTIR-350) in the spectral range between 4000 and 400 $cm^{-1}$. Pellets of about 100mg KBr powder containing finely ground powder of each sample were made in less than 1 hr before recording.

$^1$H-NMR spectra were recorded with a Fourier transform-nuclear magnetic resonance spectrometer (Bruker AMX-FT 500MHz) at 40°C in $D_2O$.

The peak molecular weights ($MW_p$) of the oxidized alginate samples were determined by gel permeation chromatography (Waters Ultrahydrogel linear column). The mobile phase consisted of aqueous sodium nitrate (0.1M) and delivered with a flow rate of 0.5mL/min. Polymer samples were dissolved in mobile phase solvent at a concentration of 0.01 g/10mL and filtered with 0.2 μm cellulose acetate filter. Pullulan (Shodex Standard P-82) in the range $5.9\times10^3$~$78.8\times10^4$ was used as standard for MW measurement. A 100 μl injection volume was used for all analyses.

*Preparation of the 2,3-dialdehydic alginate and APSs*

Sodium alginate solution (3% w/v, 200ml $H_2O$+50ml 1-propanol) was mixed after adding periodate (30% oxidation degree of the uronic acid units, 1.908g) [8] in the dark condition for 24hr at room temperature. The ethylene glycol (5ml) was added to decompose the unreacted periodate. The reaction mixture was stirred for 2 h at ambient temperature. Exclusion of light was essential for the prevention of side reaction. The final pH of the reaction medium was about 7.0. At the last step, the reaction mixture was poured with stirring into ethanol (95%, 21) and precipitate was collected by centrifugation, washed well with ethanol, and dried at 40 °C in a vacuum oven. Three different 2,3-dialdehydic alginates, which were used as starting materials for synthesizing APSs, were prepared according to the several different methods [9,10]. For the reduction of imine, $NaCNBH_3$ was used because the reduction of imine by $CNBH_3$ anion is rapid at pH values of 6~7 and the reduction of aldehyde or ketone is negligible in that pH range. To a solution of 0.404g (about 2mmol) of 30% oxidized 2,3-dialdehydic alginate (30%-CHO) dissolved in 20ml of phosphate buffer pH 7 was added 0.092g of $NaCNBH_3$. The solution was mixed with 10ml of methanol containing C8-$NH_2$, C12-$NH_2$ or C16-$NH_2$. The reaction molar ratio of alkyl amine to aldehyde on oxidized alginate was 5~7. The reductive amination was proceeded for 12hr with stirring at room temperature and then dialyzed and subsequently freeze-dried. The final products of the above procedure were 30% CHO-C8, 30% CHO-C12, and 30% CHO-C16 APS.

*X-ray diffractometry*

Wide angle X-ray diffraction patterns were recorded on a θ/θ goniometer X-ray diffractometer (model Rigaku, D/max-IIIC(3kw)) operated at the CuKα wavelength of 1.542Å at 45mA and 40kV. Measurements of diffracted intensities were made over the angular range of 5° to 60° at ambient temperature.

*Dynamic light scattering (DLS) measurement*

The dynamic light scattering measurement was performed for determining the size distribution and diffusion coefficient with an apparatus from Brookhaven Instruments Inc. equipped with He-Ne laser. The scattering angle was fixed at 90° and hydrodynamic diameter and histograms were calculated with NNLS routine and the polydispersity, $\mu_2/\Gamma^2$ was calculated by a cumulant method.

*Surface tension measurement*

The surface tensions of aqueous alginate and all APSs solutions were determined by the ring method with a tensiometer (KRÜSS Digital Tensiometer K10ST) in the concentration range of 0.02~7.6 g $L^{-1}$ at 25 °C. The c.m.c. values were estimated from the plots of surface tension *vs.* concentration of APS.

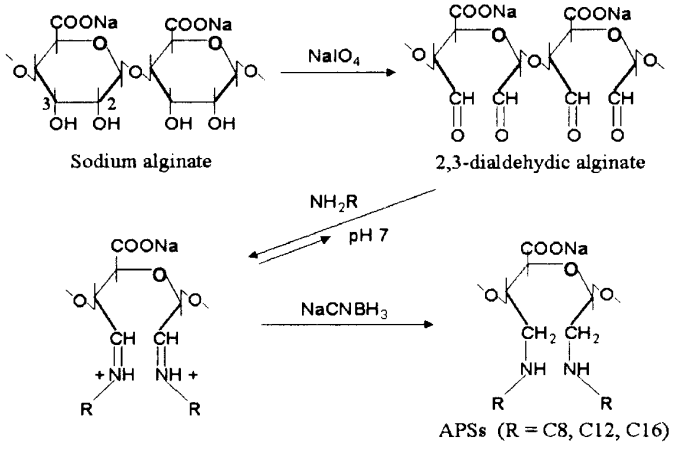
*Biodegradation test*

According to ASTM G21-70 [11], the fungi resistance of the model polymer system was observed qualitatively as judged from the visual rotating of fungus growth. The 30% CHO-C12 APS powder was placed on the surface of an agar layer and incubated

at 30°C, and approximately 80% relative humidity was maintained for 4 weeks. The fungus *Aspergillus niger* was employed, and buffered agar in the absence of polymers were used as references. The basal salt media for fungi growth consisted of the following compounds added to 1 1 of distilled water: $NaNO_3$, 3g; $K_2HPO_4$, 1g; $MgSO_4$, 0.5g; KCl, 0.5g; and $FeSO_4 \cdot 8H_2O$, 0.01g.

## Results and discussion

Aqueous solution of sodium alginate was oxidized in the dark using sodium periodate at room temperature following a procedure as shown in Scheme 1. Sodium periodate was almost quantitatively consumed in all conditions. By controlling the amount of oxidant used, a various degree of oxidized product was obtained (30%, 40%, and 50%).




**Scheme 1.** Synthesis of 2,3-dialdehydic alginate and APSs.

IR spectra of the original alginate, oxidized alginate, and APSs, show characteristic C=O bands due to symmetric and asymmetric stretching and C-H stretching bands. The C=O bands of carboxyl group at 1618 $cm^{-1}$ is broad and strong, and C=O bands of aldehydic group is not detected because of hemiacetal formation of free aldehyde groups. The increases of C-H stretching peaks at 2854 and 2917 $cm^{-1}$ are attributable to the alkyl groups of APSs. The $^1$H-NMR spectrum of 40% CHO-C12 APS shows new proton peaks compared with alginate due to alkyl chain. Additional chemical shifts are observed at 1.3 (s, b), and 0.9 ppm (s, b), which was assigned as the dodecyl chains (spectrum was not shown here).

Sodium alginate, oxidized alginate, one of the APSs, 40% CHO-C16, and hexadecylamine (C16-$NH_2$) were used for XRD analysis. The result (Figure 2) shows that sodium alginate exhibits a very small crystallinity [12]. X-ray diffraction peak at $\theta$=13.9° for the oxidized alginate samples decreases, accompanied by only very slight line broadening. Also, any sharp peak due to hexadecylamine is also absent in the 40% CHO-C16 APS (Figure 3). These results support the hydrophobization of alkylamine onto 2,3-dialdehydic alginate.

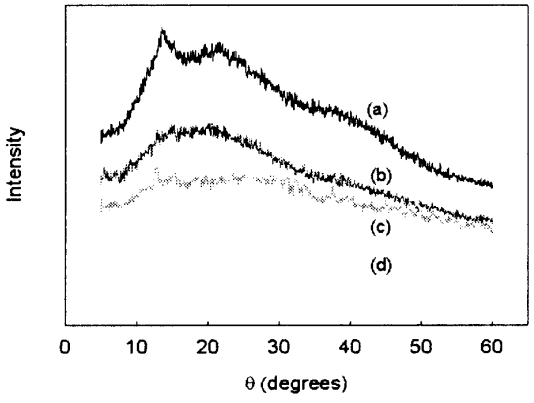



**Figure 2.** XRD analysis of (a) sodium alginate, (b) 30% CHO, (c) 40% CHO, and (d) 50% CHO

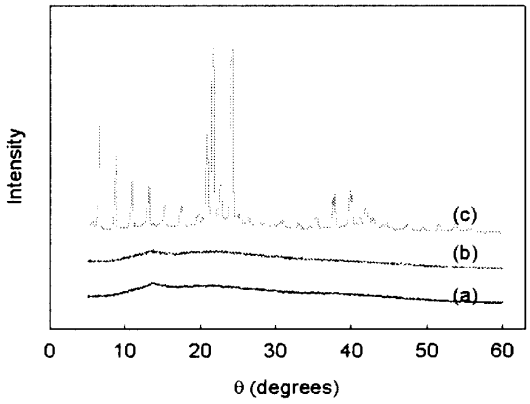



**Figure 3.** XRD analysis of (a) sodium alginate, (b) 40% CHO-C16 APS and (c) hexadecylamine (C16-$NH_2$)

The size of self-aggregates and their distribution in APS solution were measured by dynamic light scattering. Figure 4 shows the size distribution of self-aggregates in APS solution at [30% CHO-C12 APS]=0.54g/L and T=25°C. Self-aggregates of 30% CHO-C12 APS solution have the mean diameter of 223nm with a unimodal size distribution (diffusion coefficient=$0.87\times10^{-8}cm^2/sec$).

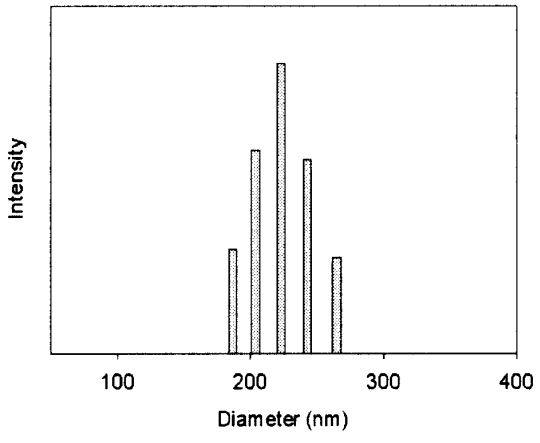



**Figure 4.** Size distribution of 30% CHO-C12 APS self-aggregates in aqueous solution measured by dynamic light scattering at [APS]=0.54g/L and T=25°C (mean diameter=223nm, diffusion coefficient=$0.87\times10^{-8}cm^2/sec$)

Polymeric micelles could have the properties such as surface activity and critical micelle concentration (c.m.c.) like monomeric micelles. The surface tensions of all APSs were below 40 $mNm^{-1}$ at their concentrations usually less than few grams per liter. This confirms the behavior of APSs as surface-active agents. However, 2,3-dialdehydic alginate and sodium alginate had no effect: the surface tensions were 66.4~70.5 $mNm^{-1}$, which are similar to that of water. Figure 5 shows the decrease of surface tension with different concentrations of 40% CHO-C8 APS, and the pattern resembles those of classic surfactants. In the case, the lowest interfacial tension (31.5 $mNm^{-1}$) was obtained at the c.m.c. value of 1.35 g $L^{-1}$. APSs derivatives show an obvious surface activity resembled those of reported polysaccharide surfactants (such as O-(2-sulfoethyl)cellulose [13], amphiphilic beechwood glucuronoxylan derivatives

[14]).

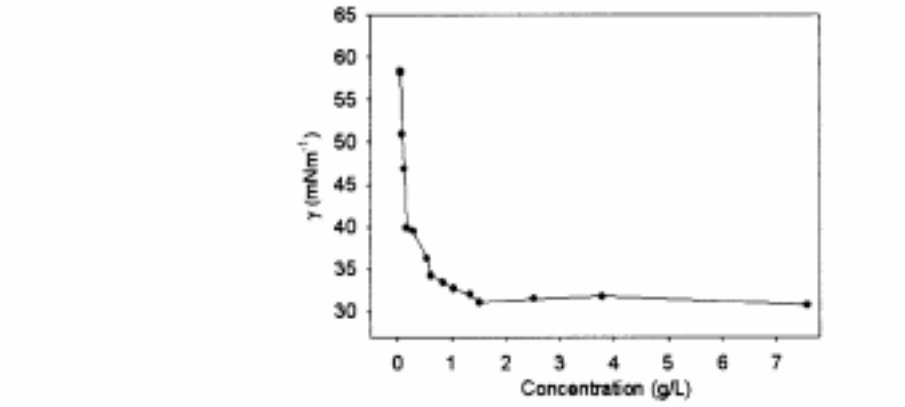



**Figure 5.** Plot of surface tension vs. concentration of the 40% CHO-C8 APS

On the biodegradability of APS, the clear evidence was derived from direct visual inspection of samples and efforts have been made to record this photographically as shown in Figure 6. Evaluation of fungal growth based on weight loss was not possible due to high swelling of APS under the experimental conditions. During the 4 week experiment, fungal growth on a control (left side) was not seen, but the 30% CHO-C12 APS (right side) developed an apparent growth. This suggested that a soil microorganism, which would cause it to disintegrate by a natural erosive force, would attack the APSs, the hydrophobically modified alginate.

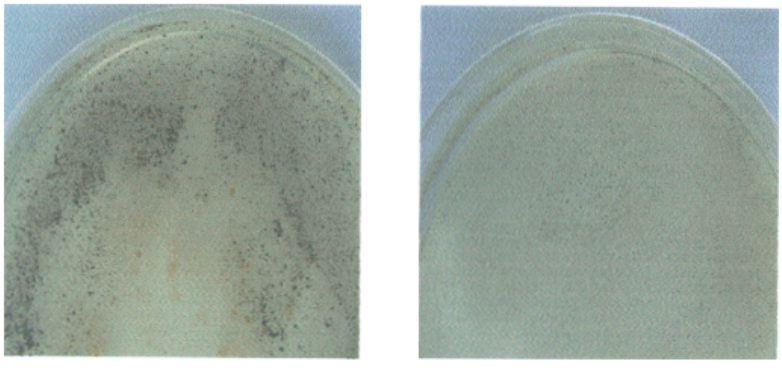


**Figure 6.** Fungus growth on the polymer surface: control-without APS (left) and 30% CHO-C12 APS (right)

## Summary and Conclusions

A new alginate-derived polymeric surfactants (APSs) were successfully prepared reductively by introduction of alkyl amine to the aldehyde group of 2,3-dialdehydic alginate, and characterized by spectral and X-ray diffractometry analysis. The synthesized 30% CHO-C12 APS provides colloidally stable self-aggregates (mean diameter of ca. 220nm) with a unimodal size distribution. The micelles of APSs have the properties such as surface activity like monomeric micelles. By a fungi resistance test, it was confirmed that the APSs would be attacked by a soil microorganism, *Aspergillus niger*. Future researches will focus on the applications of APSs as

environmentally friendly surfactants to simultaneously remove organics and divalent metal cations.

**Acknowledgements**

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