Study on the Synthesis and Characterization of Surface Activities of Hydrophilic Derivatives of β-Sitosterol

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ABSTRACT: Three kinds of hydrophilic derivatives of β-sitosterol (HPS) were synthesized from poly(ethylene glycol) (PEG) with molecular weight 1000, 2000, and 4000 by two-step reactions. The chemical structure and the distribution of isomers in HPSs were investigated by ^{1}H-NMR and Maldi-Tof, respectively. The solubility of HPS in water increased as the molecular weight of the parent PEG increased. However, when the solubility of each HPS was calculated based on the weight ratio of the β-sitosterol moiety in HPS, HPS-1000 prepared from PEG 1000 showed the highest solubility. Both the CMC and surface tension of HPS surfactant system have been found to increase with an increase in molecular weight of the parent PEG. Dynamic surface tension measurement using a maximum bubble pressure tensiometer showed that much longer time was required to reach an equilibrium value presumably due to the lower mobility of a surfactant molecule with high molecular weight. The interfacial tensions measured between HPS system and *n*-decane at 25°C were in the same order of magnitude as those exhibited between micellar solutions and nonpolar hydrocarbon oils and also found to decrease with a decrease in molecular weight of the parent PEG. The most stable foams were observed with HPS-1000 system which is consistent with that of surface tension measurement where HPS-1000 system exhibited a lower surface tension value at CMC than other two systems. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 888–895, 2012

Key words: β-sitosterol; hydrophilic derivatives; poly (ethylene glycol); surface activity

INTRODUCTION

Phytosterol means all the alcohol compounds with steroid moiety found in higher plant life and at least 44 sterols have been identified.[1] The most abundant phytosterol is β-sitosterol (24-ethyl-5-cholestene-3-ol) although β-sitosterol exists in nature as mixture including stigmasterol, campesterol and dihydrobrassicasterol which differ in side-chain configuration. β-sitosterol has demonstrated the greatest potential for the production of steroidal drugs,[2] cosmetics for healing effects on damaged skin and anti-inflammatory effects,[3] and food ingredients that function as cholesterol-lowering agents.[4] However, free form of β-sitosterol is soluble neither in water nor in various plant oils. Because of their insolubility in water and poor solubility in oil, β-sitosterol is restricted in its applications.

To overcome this problem, many studies have focused on the chemical modification of the 3-hydroxy group in β-sitosterol. The first approaches to increase the solubility of β-sitosterol in fats were carried out by esterification with fatty acids.[5–8] β-Sitosterol ester compounds were reported to have the same cholesterol-lowering effects as the parent molecule, and margarine containing a β-sitosterol ester[9] produced by transesterification of β-sitosterol with a fatty acid methyl ester derived from canola oil finally entered the United States market in 1990. On the other hand, approaches to increase the water solubility of β-sitosterol were carried out mainly by formulations with emulsifiers. For example, lecithin-emulsified micelles of β-sitosterol were reported to have a similar cholesterol-lowering effect.[10,11]

Recently, we have synthesized a new type of hydrophilic phytosterol derivative (HPS) by coupling β-sitosterol with a hydrophilic matrix by two step reactions, as described in Figure 1.[12] The first step is the synthesis of intermediate (carboxyethyl-β-sitosterol, CES), which affords carboxylic functionality to β-sitosterol, and the second step is the coupling of CES to poly(ethylene glycol) (PEG) with molecular weight of 1500. HPS was found to have the same cholesterol-lowering effects as β-sitosterol.[13] The coupling reaction between CES and PEG can produce three different compounds such as unreacted PEG, HPS (product having one sterol moieties at one end

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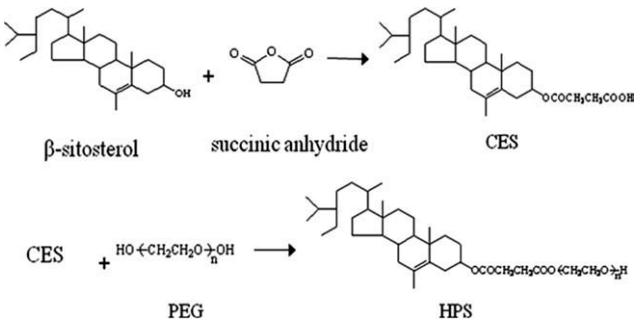

Figure 1 Synthesis of HPS.

of PEG) and Di (product having two sterol moieties at both ends of PEG) because PEG is the di-functional compound but CES is mono-functional. The preparation method for pure mono-type HPS was suggested by coupling reaction of CES and excess amount of PEG to prevent the formation of Di and following purification process to remove unreacted PEG.[12] Since HPS is composed of hydrophilic PEG with hydrophobic moiety (β-sitosterol) at only one end, the potential application of HPS as a surfactant is also expected.

In this study, three kinds of mono-type HPSs were synthesized from PEG with molecular weight 1000, 2000, and 4000 by reacting CES with 5 molar excess of corresponding PEG and removing unreacted PEG by extraction. For comparison, di-type HPSs which have two sterol moieties at both end of PEG were also synthesized from corresponding PEG. The chemical structure and the distribution of isomers of HPSs were investigated by ^{1}H-NMR and Maldi-Tof, respectively. Surface activities of HPSs were also measured and discussed as a function of molecular weight of the parent PEG. This study is the first example, which demonstrates the potential application of the hydrophilic derivatives of phytosterol as surface active compounds.

EXPERIMENTAL

Materials

β-Sitosterol, PEG (MW = 1000, 2000, and 4000), succinic anhydride, 1,3-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were purchased from Aldrich and used without further purification. β-Sitosterol contains 20–30% of campersterol and 10–30% of dihydrobrassicasterol.

^{1}H-NMR was obtained by Spectrometer FT-NMR (500 MHz) of Bruker using $CDCl_3$ as a solvent. Voyager Biospectrometry Workstation (Applied Biosystem) was used for the measurement of Matrix-Assisted Laser Desorption Ionization Mass Spectrometry (Maldi-Tof).

Preparation of CES

41.5 g (0.10 mol) of β-sitosterol and 15.0 g (0.15 mol) of succinic anhydride are dissolved in 200 mL of toluene, and 2.5 g (0.02 mol) of DMAP was added. Excess amount of succinic anhydride was used to ensure that hydroxy terminals of β-sitosterol were completely reacted. Reaction mixture was refluxed for 6 h. After confirming the completion of the reaction with thin layer chromatography (TLC), the reaction mixture was precipitated into 400 mL of hexane, and crude product was recovered by filtration. After dryness, recrystallization in ethanol afforded 41.7 g of intermediate compound (yield, 81%). The structure of CES was confirmed by ^{1}H-NMR in $CDCl_3$.

Preparation of HPS-1000

100.0 g of PEG having a molecular weight of 1000, 5.2 g (25 mmol) of DCC, and 0.2 g (1.3 mmol) of DMAP were dissolved in 100 mL of methylene chloride (MC). 10.3 g (20 mmol) of CES predissolved in 100 mL of MC was then added dropwise to the reaction mixture at 30°C. The reaction continued at 30°C until the CES peak disappeared in TLC. Dicyclohexylurea was removed by filtration, and filtrate was extracted with distilled water containing 5% NaCl, and with distilled waster two more times to completely remove unreacted PEG. After evaporation of organic layer, crude product was dissolved in 100 mL of isopropyl alcohol and hexane (1 : 3 by volume) mixture at 40°C and stored at 4°C overnight. After filtration and dryness, 8.2 g of pure HPS-1000 was obtained and the structure of HPS was confirmed by ^{1}H-NMR in $CDCl_3$.

HPSs with different chain lengths were prepared with the same procedure and named as HPS-2000 and HPS-4000, respectively with corresponding PEG. Only difference is that 1 : 2 and 1 : 1 mixture of isopropyl alcohol, and hexane were used for HPS-2000 and HPS-4000, respectively, for the final purification.

Preparation of Di-1000

Di was prepared by the esterification of PEG in the presence of excess amount of CES.

PEG 7.78 g (7.78 mmol) of PEG (MW = 1000), 3.69 g (17.89 mmol) of DCC, 0.11 g (0.89 mmol) of DMAP, 10 g (19.46 mmol) of CES were dissolved in 100 mL of MC, and the reaction continued at 30 for 6 h. Dicyclohexylurea was removed by filtration, and filtrate was extracted with water containing 5% NaCl, and with distilled waster. After evaporation of organic layer, crude product was dissolved in 50 mL of isopropyl alcohol and hexane (1 : 5 by volume) mixture at 40°C and stored at 4°C overnight. After filtration and

dryness, 3.2 g of pure Di-1000 was obtained and the structure was confirmed by ^{1}H-NMR in $CDCl_3$.

Di with different chain lengths were prepared with the same procedure and named as Di-2000 and Di-4000, respectively with corresponding PEG.

Solubility test of HPS

The solubility was visually determined after 2 g of HPS in 4 mL of water was stirred at 35°C for 2 h. When the solution became clear, it kept at 4°C for 24 h. If HPS was not soluble at 35°C or the precipitation appeared during the storage at 4°C, 0.2 mL of water added and the same procedure was repeated until the solution appeared clear. Critical concentration at 4°C was defined by the maximum concentration where the solution was visually clear.

Measurement of surface activities

The surface tension of an aqueous surfactant solution was measured using a Du Nuoy ring tensiometer with a platinum ring (Kruss K100, Germany) at 25°C. Dynamic surface tensions for shorter time periods were measured by a bubble pressure tensiometer (Kruss BP2, Germany), where the range of bubble life time used was from 5 to 60,000 ms. A spinning drop tensiometer (Kruss, Site 04, Germany) equipped with a video camera (Sony SSC-DC374, Japan) was utilized to measure the interfacial tension between surfactant solution and *n*-decane oil at 25°C.

A drop-shape analysis system (Kruss DSA100, Germany) was used to measure a contact angle at 25°C by forming a drop of surfactant solution on a glass microslide. Foam stability was measured by using a foam test apparatus (IFAC FoamScan, Germany) where average foam formation rate was obtained based on the time required for foam to reach the 20-cm mark above from an initial 0-cm marked position and foam stability was recorded by measuring foam decay with time. Reproducibility was confirmed by running each system twice or more. Water used for sample preparation was ultrapure having been double distilled and passed through a Nanopure (Sybron-Brinkman Inc.) ion exchange system.

RESULTS AND DISCUSSION

Preparation and characterization of HPS

The intermediate, CES, was synthesized according to the reported method[13–15] with minor modification. The chemical structure of CES was confirmed by ^{1}H-NMR studies. As described in Figure 2(a,b), proton of 3-position at 3.5 ppm (b in (a)) of free β-sitosterol has shifted to 4.6 ppm in (b in B), since vicinal hydroxy group has changed into ester group.

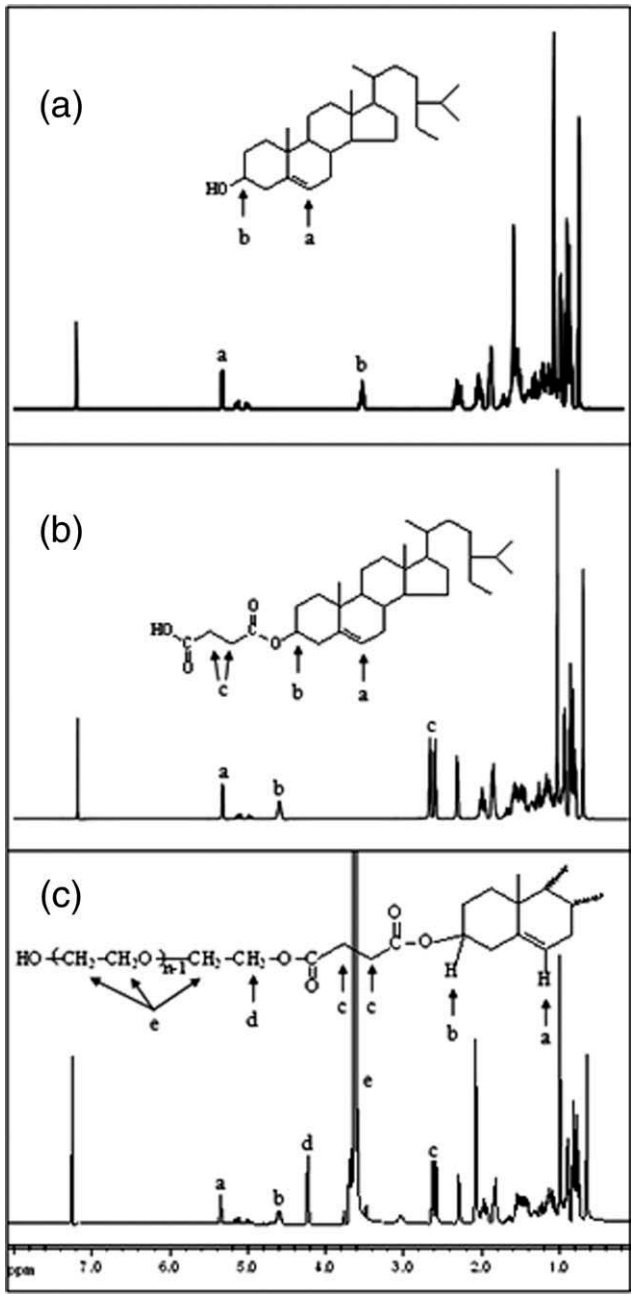

Figure 2 ^{1}H-NMR spectra of β-sitosterol (a), CES (b), and HPS-1000 (c).

The absence of succinic anhydride in CES, which appears at 3.2 ppm if remained, was also confirmed by H-NMR.

There are many known methods to prepare ester compounds by coupling OH and COOH groups. In this study, the combination of DCC (dehydrating agent) and DMAP (acylation catalyst) were used for the preparation of HPS, and the reactions continued until CES completely disappeared in TLC.

As described in Figure 2(c), ^{1}H-NMR spectrum of the product showed a remarkable peak at 3.5–3.7 ppm (e), which is assigned to methylene protons of PEG. The most characteristic peak appeared at

TABLE I
DS Values and Molecular Weight of PEG, HPS, and Di

		DS[a]	Mn[b]	Mw[b]	PDI[b]
PEG	1000	–	1086.5	1101.9	1.01
	2000	–	2087.8	2120.9	1.02
	4000	–	3579.1	3622.6	1.01
HPS	1000	1.02	1571.1	1602.4	1.02
	2000	1.06	2497.2	2539.7	1.02
	4000	0.92	3995.9	4113.1	1.03
Di	1000	2.01	2033.9	2053.1	1.01
	2000	1.94	2946.6	3030.6	1.03
	4000	1.88	4408.0	4532.8	1.03

[a] Measured by ^{1}H-NMR.
[b] Measured by Maldi-Tof.

4.3 ppm (d) can be assigned to terminal methylene protons of PEG coupled with CES, and the appearance of it is considered to be direct evidence of esterification of CES with PEG. The integration ratio of peak "a," "b," "c," and "d" was observed to correspond to the ideal ratio (1 : 1 : 4 : 4).

The coupling reaction between CES and PEG can produce three different compounds such as unreacted PEG, HPS, and Di (product having two sterol moieties at both ends of PEG) because PEG is the di-functional compound but CES is mono-functional. In this study, pure mono-type HPS was synthesized by coupling reaction of CES and excess amount (five times in equivalent ratio) of PEG to prevent the formation of Di and following purification process to remove unreacted PEG, as described in experimental section.

From ^{1}H-NMR data, DS (degree of substitution), which means average number of sterol moieties in HPS, can be calculated according to the following equation:[12]

$$\begin{aligned} \mathrm{DS} &= \frac{\text{integration equivalent to one H in sterol moiety of HPS}}{\text{integration equivalent to one H in PEG chain of HPS}} \\ &= (c/4)/\{(d+e)/4n\} \\ &= n \cdot c/(d+e) \end{aligned}$$

where n is the degree of polymerization of PEG, and c, d, and e are the integrations of each peak assigned in Figure 2(c).

As summarized in Table I, the DS values of HPSs were close to 1.0, and 2.0 for Di. However, unity of DS value of HPS does not necessarily imply that each PEG chain contains only one sterol moiety. DS is also close to unity if the product contains same amount of unreacted PEG and Di.

Further studies on the distribution of isomers in HPS were carried out by Maldi-Tof. Figure 3 shows Maldi-Tof spectra of PEG, HPS, and Di with different chain lengths. Each peak has intervals of 44, which is equivalent to the mass of monomeric unit of PEG, and all spectra shows a narrow range in molecular weight. Spectra of HPSs ((d), (e), and (f)) displays identical pattern with those of corresponding PEGs ((a), (b), and (c)), except that the molecular weight (m/z) of HPS shifts to the higher m/z to the extent of approximately 500 m/z compared to that of PEG. Theoretically, the molecular weight of HPS should be higher by 496 g/mol than that of the parent PEG. Spectra of Di ((g), (h), and (i)), likewise, displays a displacement to the higher m/z to the extent of approximately 1000 m/z compared to that of PEG. These results strongly indicate that the HPSs prepared in this study are pure mono-type derivatives.

Hydrophilic properties of HPS

The water-solubility and hydrophilic-lipophilic balance (HLB) numbers, which were calculated according to the Griffin method,[16,17] are summarized in Table II. HPSs are well soluble in water even at 4°C, and the solubility of HPSs slightly increases as the molecular weight of the parent PEG and HLB number increase. However, even though the HLB value of HPS-4000 is higher than that of HPS-2000, we did not observe a significant difference in solubility, which is considered to be caused by the higher molecular weight of HPS-4000 compared to that of HPS-2000. On the other hand, Di was not soluble in water even at 10 mg/mL regardless of molecular weight of the parent PEG. It is clear that introduction of two bulky hydrophobic groups (β-sitosterol) into both ends of PEG limits water-solubility of Di.

Considering the application of HPS, it is also important to evaluate the solubility based on the β-sitosterol moiety in HPS, which can be calculated from the following equation:

$$\text{Weight ratio of β-sitosterol moiety in HPS} = 416(\mathrm{g/mol})/\mathrm{Mn(g/mol)}$$

where 416 means molecular weight of β-sitosterol and M_n means number average molecular weight of HPS which is obtained from Madi-Tof measurement as described in Table I.

As shown Table II, based on the β-sitosterol moiety of HPS, the solubility of HPS-1000 is much higher than those of HPS-2000 or 4000.

Surface activity of HPS

One of the most important parameters characterizing a surfactant is its critical micelle concentration (CMC). The CMC can be determined by means of many experimental methods such as surface tension, density, solubility, turbidity, osmotic pressure, electrical conductivity, light scattering properties, detergency, and so forth. During this study, the CMC

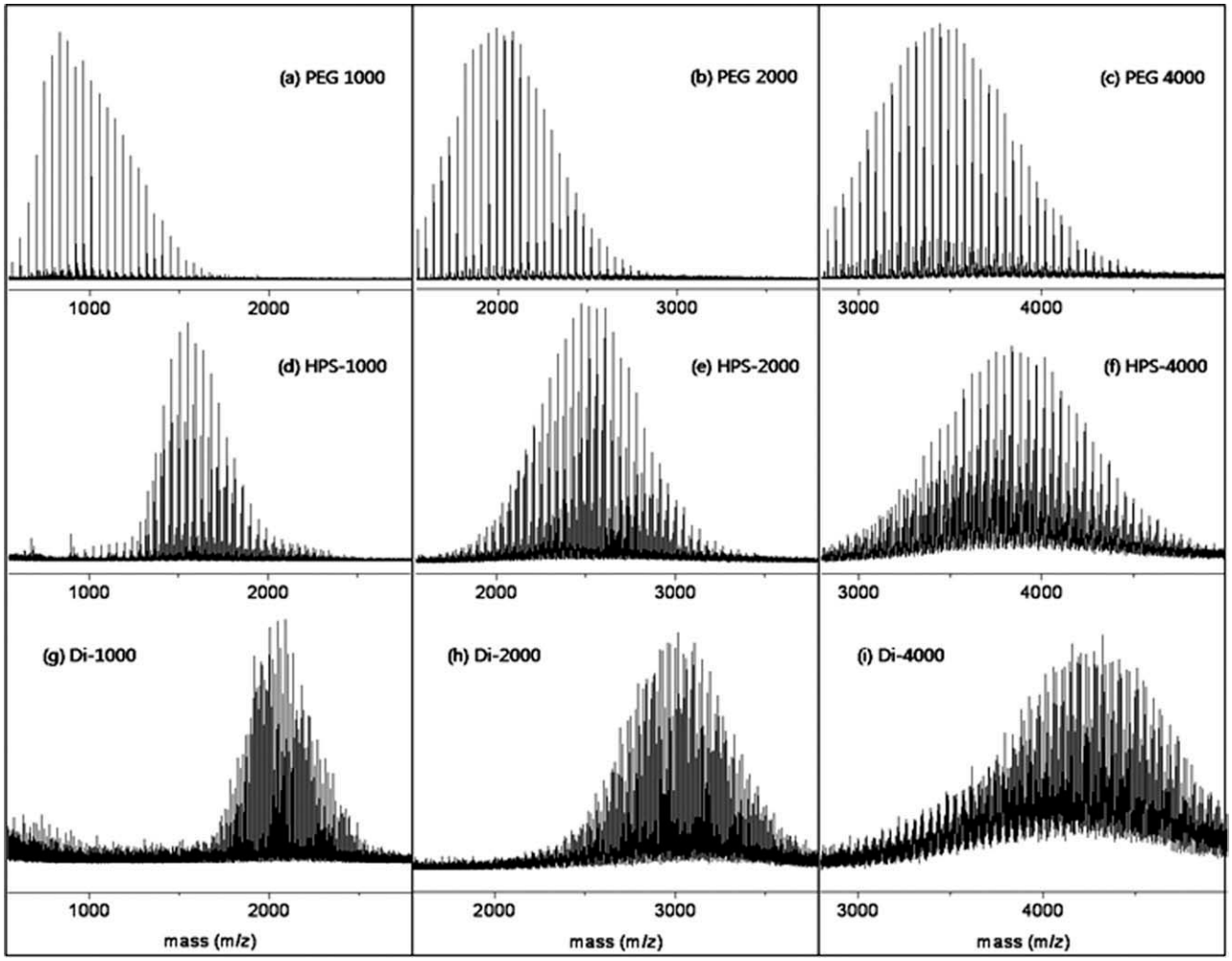

Figure 3 Maldi-Tof spectra of PEG 1000 (a), 2000 (b), 4000 (c), HPS-1000 (d), -2000 (e), -4000 (f), Di-1000 (g), -2000 (h), and -4000 (i).

was determined by measuring the surface tension of a surfactant as a function of concentration. The CMC was considered as the concentration beyond which the surface tension of the aqueous solution does not change any more. In addition to CMC, other physical properties such as surface tension, interfacial tension, contact angle, and foam stability were measured at 25°C and the results are summarized in Table III.

As shown in Figure 4 and Table III, both the CMC and surface tension at the CMC are found to increase with increasing the hydrophilicity of a surfactant. For example, the CMC's of HPS-1000, 2000, and 4000 surfactant systems are 4.8410×10^{-5} mol/L, 4.9110×10^{-5} mol/L, and 5.0310×10^{-5} mol/L respectively. Also the corresponding surface tensions at their CMC conditions are 45.41 mN/m, 49.69 mN/m, and 53.03 mN/m, respectively.

It is not surprising to observe that the surface tension of an aqueous solution of HPS surfactant increases with an increase in molecular weight of the parent PEG. This result may be attributed to the fact that an increase of the hydrophilic portion of the surfactant results in a decrease in its concentration at the air/water interface and thus the area per molecule increases. The increase in surface tension with an increase in the chain length of ethylene oxide (EO) is a well-known phenomenon in conventional nonionic surfactants.[18,19] It is worth pointing out that with comparable hydrocarbon chain lengths

TABLE II
Water-Solubility at 4°C and HLB Values of HPS

	Solubility		HLB
	Critical concentration[a] (mg of HPS/mL of water)	Critical concentration[a] (mg of β-sitosterol moiety in HPS/mL of water)	
HPS-1000	313	83	13.2
HPS-2000	370	63	15.9
HPS-4000	385	42	17.7

[a] Maximum concentration where the solution becomes visually clear.

TABLE III
Physical Properties of HPS Measured at 25°C

Code	CMC (g/L)	CMC (mol/L)	Surface tension[a] (mN/m)	Interfacial tension[b] (mN/m)	Half-life[c] (s)	Contact angle[d] (°)
HPS-1000	0.0759	4.84×10^{-5}	45.41	0.3048	2526	51.00 ± 0.53
HPS-2000	0.1218	4.91×10^{-5}	49.69	0.4235	1226	41.10 ± 0.60
HPS-4000	0.1914	5.03×10^{-5}	53.03	0.4821	850	40.73 ± 0.05

[a] Surface tension at CMC.
[b] Measured between 1 wt % surfactant solution and *n*-decane oil.
[c] Time required for initial foam volume to decrease by 50%.
[d] Measured with 1 wt % surfactant solution.

CMC's are much lower for nonionic surfactants. The reason is that electrical repulsion between negatively charged hydrophilic groups strongly opposes micelle formation for anionic surfactants.

Dynamic surface tension measurement using a maximum bubble pressure tensiometer showed a decrease in the surface tension of the aqueous surfactant solution with an increase in surfactant concentration in the solution. In addition, much longer time was required to reach an equilibrium value compared with conventional nonionic or ionic surfactants presumably due to the lower mobility of a surfactant molecule with high molecular weight. As shown in Figure 5, the surface tension of the HPS-2000 surfactant solution decreased as the surfactant concentration increased and equilibrium surface tension value of 45.41 mN/m was never reached even at high concentrations. This result indicates that any depletion of HPS-2000 surfactant molecules from the air/water interface will not be replenished by an instantaneous diffusion of molecules from the bulk aqueous solution presumably due to lower mobility of surfactant molecule. The same trend in dynamic surface tension measurement was observed with other surfactants of HPS-1000 and HPS-2000, and the similar results were reported in other surfactant systems.[20,21]

Interfacial tensions were measured as a function of time for *n*-decane drops brought into contact with 1 wt % surfactant solutions at 25°C. As Figure 6 indicates, the tension for the system of HPS-4000 dropped over a period of about 10 min to an equilibrium value of 0.4821 mN/m. For the HPS-2000 system, the interfacial tension ultimately reached a value of 0.4235 mN/m in less than 7 min, which was somewhat lower than HPS-2000 system. On the other hand, the interfacial tension between 1 wt % HPS-1000 and *n*-decane fell more rapidly and finally reached a limiting value of about 0.3048 mN/m in less than 10 min.

Figure 6 shows that the interfacial tension between HPS system and *n*-decane decreases with a decrease in molecular weight of the parent PEG. It is well-known that the CMC decreases and the aggregation number increases with decreasing the chain length of hydrophilic portion and with increasing temperature since both these effects cause the surfactant to become less hydrophilic in conventional nonionic surfactants.[18,19] It is also worthy to mention that the interfacial tensions measured between HPS system

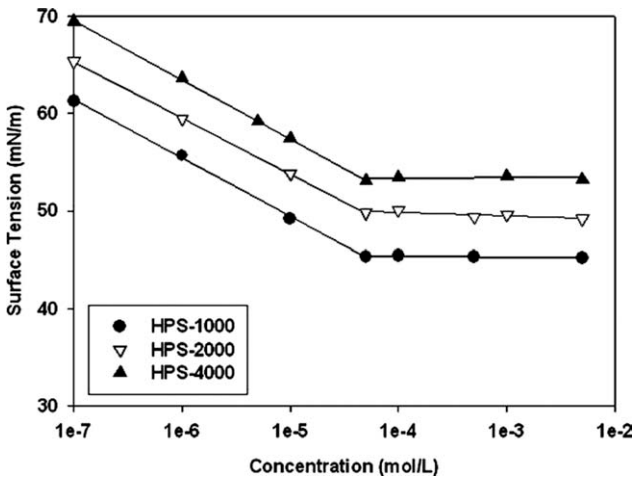

Figure 4 CMC measurement using a Du Nuoy ring tensiometer at 25°C.

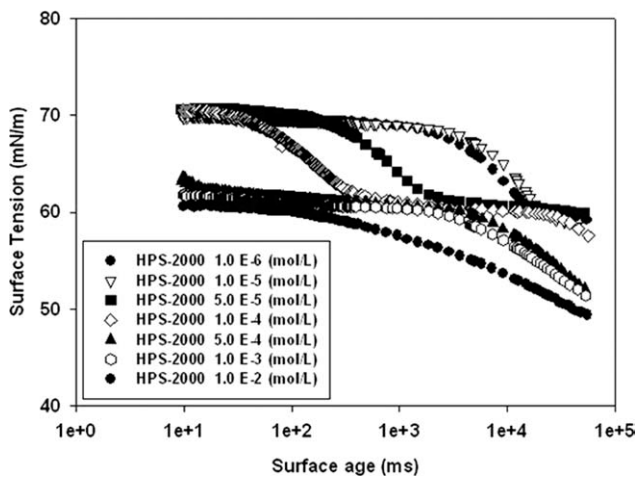

Figure 5 Dynamic surface tension of HPS-2000 measured by a maximum bubble pressure tensiometer at 25°C.

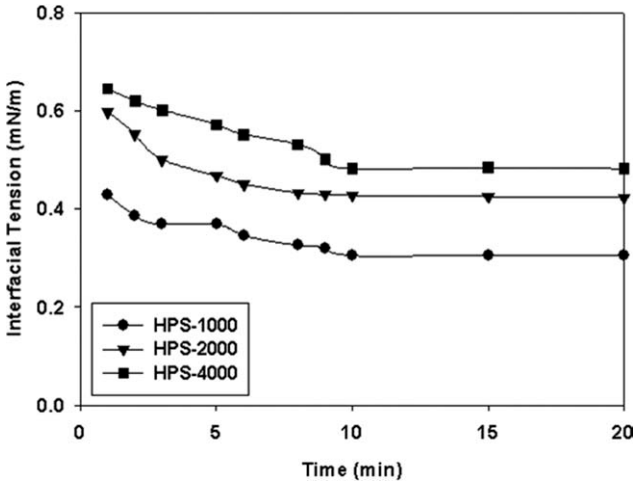

Figure 6 Dynamic interfacial tension measured between 1 wt % aqueous solution and *n*-dacane oil at 25°C using a spinning drop tensiometer.

and *n*-decane oil are in the same order of magnitude as those exhibited between micellar solutions and nonpolar hydrocarbon oils.[22–24]

The stability of foams is important in a variety of applications. Foams are undesirable in many practical applications, such as in the case of automatic dishwasher detergents, paints, food products, distillation columns, sewage plants, and many industrial processes where additives are used to eliminate or control the foam. However, in some practical applications, where copious and long-lasting foams are desirable such as in the case of hand dish washing detergents, soaps, shampoos, shaving creams, beer, bubble bath, and fire-fighting agents, additives are used to increase foam stability.[25,26]

There are various ways by which additives can help to stabilize foams such as: increasing the elasticity of the foam film; slowing down the drainage of liquid in the lamellae; decreasing the diffusion of gas across the lamellae; increasing the thickness of the electrical double layer; increasing the surface and bulk viscosity of the foam film. Although some additives may contribute by one particular mechanism, others may offer a stabilizing effect with several mechanisms operating simultaneously.[27]

Surface active organic compounds are the most commonly used foam additives in practical applications. These organic additives typically stabilize foam by enabling the surfactant molecules to form a closely packed foam film that exhibits more elasticity and more resistance to drainage, and consequently is less susceptible to external disturbance. Among the best known from this class of additive are fatty alcohols, fatty acids, alkanolamides, amine oxides, and various other surfactants.[28–30]

The stability of foams made with aqueous surfactant solutions against coalescence and diffusion expansion of bubbles is characterized by the variation of the dispersity with time. In foams that are in contact with the atmosphere, the whole volume (or height) of the foam diminishes with time. This process takes place simultaneously with the internal foam collapse, which does not change the foam volume. The time for complete destruction (or the disappearance of a certain portion of a column) is a parameter widely used as a characteristic of foam stability. In this study, foam stability for 1 wt % surfactant solution was studied at 25°C by measuring a half-life, which corresponds to the time required for initial foam volume to decrease by 50%.

The half-life of a surfactant solution has been found to decrease with an increase in molecular weight of the parent PEG, as summarized in Table III. The most stable foams were observed with HPS-1000 system since a larger value of half-life indicates more stable foams. This result is consistent with that of surface tension measurement where HPS-1000 system exhibited a lower surface tension value at CMC than other surfactant systems. Obviously, the introduction of a surfactant into a liquid significantly changes the properties of gas dispersions and liquid films. The surface active materials present in the aqueous solution are preferentially adsorbed at the surface and lower the surface tension at the gas/liquid interface, facilitate the dispersion of gas and reduce the size of bubbles, and change the velocity and regime of bubble rise.[31–33] Therefore, the surfactant system of low surface tension is more efficient against coalescence of bubbles and foam collapse.

Contact angle for 1 wt % surfactant solution was measured at 25°C by forming one drop of aqueous surfactant solution on a glass slide and determined by the angle formed between planes tangential to the surfaces of the solid and liquid at the wetting perimeter. A contact angle less than 90° (low contact angle) usually indicates that wetting of the surface is very favorable, and the fluid will spread over a large area of the surface. Contact angles greater than 90° (high contact angle) generally means that wetting of the surface is unfavorable so the fluid will minimize contact with the surface and form a compact liquid droplet. As summarized in Table III, a decrease in the contact angle of the aqueous solution was observed with an increase in molecular weight of the parent PEG. This result indicates that HPS-4000 is a better wetting agent than HPS-1000 and HPS-2000.

CONCLUSION

Three kinds of HPSs were synthesized from PEG with molecular weight 1000, 2000, and 4000 by reacting CES with 5 molar excess of corresponding PEG and removing unreacted PEG by extraction. All

HPSs are soluble in water, and HPS-1000 showed the highest solubility based on the β-sitosterol moiety in HPS.

Both the CMC and surface tension of HPS surfactant system have been found to increase with increasing the hydrophilicity of a surfactant. For example, the CMC's of HPS-1000, 2000, and 4000 surfactant systems are 4.8410×10^{-5} mol/L, 4.9110×10^{-5} mol/L, and 5.0310×10^{-5} mol/L, respectively. Also the corresponding surface tensions at CMC conditions are 45.41 mN/m, 49.69 mN/m, and 53.03 mN/m, respectively. Dynamic surface tension measurement using a maximum bubble pressure tensiometer showed a decrease in the surface tension of the aqueous surfactant solution with an increase in surfactant concentration in the solution. In addition, much longer time was required to reach an equilibrium value compared with conventional nonionic or ionic surfactants presumably due to the lower mobility of surfactant molecule with high molecular weight. The interfacial tensions measured between HPS system and *n*-decane at 25°C were in the same order of magnitude as those exhibited between micellar solutions and nonpolar hydrocarbon oils and also found to decrease with a decrease in molecular weight of the parent PEG.

The most stable foams were observed with HPS-1000 system, which is consistent with that of surface tension measurement where HPS-1000 system exhibited a lower surface tension value at CMC than other two systems. A decrease in the contact angle of the aqueous solution was observed with an increase in molecular weight of the parent PEG which indicates that HPS-4000 is a better wetting agent than HPS-1000 and HPS-2000. The potential application of HPS as a surface active material with biological activities of β-sitosterol such as healing effects on damaged skin or anti-inflammatory effects is expected.

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