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Reactivity of a condensed–type lignin model compound in the Mannich reaction and preparation of cationic surfactant from sulfuric acid lignin

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Abstract The chemical conversion of phenolized sulfuric acid lignin (P-SAL), prepared from sulfuric acid lignin (SAL) by phenolation with sulfuric acid catalyst, to novel cationic surfactant was investigated. To elucidate the chemical reactivity of the P-SAL to a Mannich reaction, 1-guaiacyl-1-*p*-hydroxyphenylethane (**I**) as a simple phenolized sulfuric acid lignin model compound was reacted with dimethylamine and formaldehyde. Quantitative analysis of the products by gas-liquid chromatography suggested that the *p*-hydroxyphenyl nucleus was more reactive than the guaiacyl nucleus. The Mannich reaction of SAL with dimethylamine did not yield a soluble cationic surfactant, but P-SAL produced water-soluble cationic surfactant in a quantitative yield. The Mannich reaction products (MP-SAL) of P-SAL had 1,3-dimethylaminomethyl groups/C_9-C_6. The results of the surface tension measurements showed that the decrease in surface tension of MP-SAL was much larger than that of lignosulfonate as a commercial surfactant from lignin.

Key words Lignin · Mannich reaction · Cationic surfactant · Acid hydrolysis lignin · Lignin model compounds

Introduction

From the standpoint of biomass utilization, acid-catalyzed saccharification of woody materials is one of the more effective methods. The process with concentrated sulfuric acid has the advantage of producing a higher yield of hydrolysis monosaccharides, although it also produces large quantities of less-reactive sulfuric acid lignin as a by-product. Softwood sulfuric acid lignin is characterized by condensed structures formed by intermolecular dehydration between the benzylic carbons and the 6-positions of the guaiacyl nuclei.[1,2] Thus, sulfuric acid lignin has extremely low reactivity. One of the key considerations when developing this saccharification process is finding effective ways to utilize sulfuric acid lignin.

During the course of basic studies on the chemical structures of sulfuric acid lignin, it has been found that condensed aromatic nuclei with a diarylmethane structure are easily exchanged with phenol in the presence of a sulfuric acid catalyst.[3] As a result, the reactivity of phenolized sulfuric acid lignin (P-SAL) is enhanced because a reactive *p*-hydroxyphenyl moiety is introduced at the side chain α-position instead of condensed-type aromatic nuclei. During previous investigations, P-SAL was converted to water-soluble lignosulfonate[4,5] and a strongly acidic cation-exchange resin[6] in quantitative yields. Other direct conversions of acid hydrolysis lignin into functional materials have been attempted as well. Tai et al.[7] prepared an anion exchanger by chloromethylation and subsequent amination. Watanabe et al.[8] showed that radical sulfonation of acid hydrolysis lignin with sodium sulfite and oxygen enabled the preparation of soluble lignosulfonate.

In this study, the chemical conversion of P-SAL to novel cationic surfactant, which has not been prepared from sulfuric acid lignin, by the Mannich reaction was investigated. Cationic surfactant was used on fibers as a softening and antistatic agent, corrosion inhibitor, emulsifier for asphalt, germicide, flotation agent, and so on.[9,10] A condensed-type guaiacyl lignin model compound was reacted with formaldehyde and dimethylamine to acquire basic knowledge of the reactivity of aromatic nuclei in a Mannich reaction.

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Experimental

Synthesis of 1-guaiacyl-1-*p*-hydroxyphenylethane (**I**)

Compound **I** was prepared as previously described.[11]

Mannich reaction of **I**

Aqueous (50%) dimethylamine (0.63 ml, 7.0 mmol) and 37% aqueous formaldehyde (0.5 ml, 6.2 mmol) were added to a cooled (0°C) stirred mixture of **I** (500 mg, 2.0 mmol), acetic acid (12.5 ml), and dioxane (12.5 ml). The mixture was then heated at 50°C for 4 h. After adjusting to pH 9 with 2 N NaOH, the reaction mixture was extracted with ethyl acetate. The ethyl acetate solution was dried over sodium sulfate and then concentrated under reduced pressure. Products were separated by silica-gel column chromatography with *n*-hexane and acetone (5:1 v/v) to give three compounds (**II**, **III**, **IV**).

II: yield: 9.8%; MS *m/z*: 301 (M^+); ^{1}H NMR δ: 1.55 (3H, d, $J = 8$ Hz; CH_3), 2.29 [6H, s; $N(CH_3)_2$], 3.57 (2H, s; CH_2), 3.78 (3H, s; OCH_3), 3.97 (1H, q, $J = 8$ Hz; CH), 6.65 (1H, d, $J = 2$ Hz; aromatic H), 6.70 (1H, q, $J = 2 + 9$ Hz; aromatic H), 6.74 (1H, d, $J = 9$ Hz; aromatic H), 6.76 (1H, d, $J = 2$ Hz; aromatic H), 6.82 (1H, d, $J = 9$ Hz; aromatic H), 7.02 (1H, q, $J = 2 + 9$ Hz; aromatic H), 7.47 (2H, s, 2 × OH); ^{13}C-NMR δ: 22.5 (CH_3), 43.6 (CH), 44.6 [$N(CH_3)_2$], 55.9 (OCH_3), 63.1 (CH_2), 110.5, 114.2, 115.9, 120.2, 121.8, 127.6, 127.7, 137.2, 139.3, 143.9, 146.5, 156.3.

III: yield: 8.2%; MS *m/z*: 301 (M^+); ^{1}H-NMR δ: 1.54 (3H, d, $J = 8$ Hz; CH_3), 2.31 [6H, s; $N(CH_3)_2$], 3.60 (2H, s; CH_2), 3.79 (3H, s; OCH_3), 3.96 (1H, q, $J = 8$ Hz; CH), 6.44 (1H, s; aromatic H), 6.63 (1H, s; aromatic H), 6.75 (2H, d, $J = 9$ Hz; aromatic H), 6.89 (2H, s; 2 × OH), 7.02 (2H, d, $J = 9$ Hz; aromatic H); ^{13}C-NMR δ: 22.4 (CH_3), 43.5 (CH), 44.5 [$N(CH_3)_2$], 56.0 (OCH_3), 62.5 (CH_2), 110.9, 115.4, 119.5, 121.7, 128.6, 137.5, 138.7, 145.3, 147.7, 154.5.

IV: yield: 2.5%; MS *m/z*: 358 (M^+); ^{1}H-NMR δ: 1.54 (3H, d, $J = 8$ Hz; CH_3), 2.31 [6H, s; $N(CH_3)_2$], 2.33 [6H, s; $N(CH_3)_2$], 3.58 (2H, s; CH_2), 3.61 (2H, s; CH_2), 3.81 (3H, s; OCH_3), 3.94 (1H, q, $J = 8$ Hz; CH), 6.42 (1H, s; aromatic H), 6.62 (1H, s; aromatic H), 6.75 (1H, d, $J = 9$ Hz; aromatic H), 6.76 (1H, d, $J = 1$ Hz; aromatic H), 7.01 (1H, q, $J = 1 + 9$ Hz; aromatic H), 7.45 (2H, s; 2 × OH); ^{13}C-NMR δ: 22.5 (CH_3), 43.5 (CH), 44.5 [$N(CH_3)_2$], 56.0 (OCH_3), 62.5 (CH_2), 63.0 (CH_2), 110.9, 115.9, 119.5, 121.7, 127.7, 137.4, 145.4, 147.8, 156.2.

A solution of **I** (100 mg, 0.41 mmol), large excess dimethylamine (22.0 mmol), and formaldehyde (22.0 mmol) in dioxane (2.5 ml) was heated at 50°C for 4 h. After adjusting to pH 9 with 2N NaOH, the reaction mixture was extracted with ethyl acetate. The ethyl acetate solution was dried over sodium sulfate and concentrated under reduced pressure to give crude products, which were then separated by silica-gel column chromatography with methanol to isolate **V**.

V: yield 2.3%; MS *m/z*: 415 (M^+); ^{1}H-NMR δ: 1.55 (3H, d, $J = 8$ Hz; CH_3), 2.26 [12H, s; 2 × $N(CH_3)_2$], 2.30 [6H, s; $N(CH_3)_2$], 3.51 (4H, s; 2 × CH_2), 3.58 (2H, s; CH_2), 3.80 (3H, s; OCH_3), 3.94 (1H, q, $J = 8$ Hz; CH), 6.41 (1H, d, $J = 2$ Hz; aromatic H), 6.62 (1H, d, $J = 2$ Hz; aromatic H), 6.84 (2H, s; aromatic H); ^{13}C-NMR δ: 22.4 (CH_3), 43.4 (CH), 44.5 [$N(CH_3)_2$], 44.8 [2 × $N(CH_3)_2$], 55.9 (OCH_3), 60.5 (2 × CH_2), 62.8 (CH_2), 110.8, 119.3, 121.7, 122.9, 128.0, 136.5, 137.6, 145.3, 147.6, 154.9.

Gas chromatography

About 10 mg of the Mannich reaction products was dissolved in 10 ml pyridine. Then 50 μl of an *N,O*-bis(trimethylsilyl)trifluoroacetamide was added to 30 μl of the reaction solution and allowed to stand at room temperature for 1 h. The analysis was performed with 3 μl of the silylated sample. Apocynol was used as an internal standard.

The trimethylsilane (TMS) derivatives were analyzed by gas chromatography using a GL Sciences GC-353 gas chromatograph under the following conditions: column: a capillary column (GL Sciences) TC-1 60 m × 0.25 mm i.d.; injection temperature 200°C; column temperature 150°–280°C (programmed temperature 2.0°C/min from 150°C to 280°C); carrier He; detector FID. Apocynol: retention time (rt) 15.4 min. **I**: rt 44.3 min, correction factor (cf) 0.70 mol. **II**: rt 52.7 min, cf 0.65 mol. **III**: rt 53.2 min, cf 0.64 mol. **IV**: rt 60.3 min, cf 0.58 mol. **V**: rt 67.8 min, cf 0.54 mol.

Sulfuric acid lignin

Sulfuric acid lignin (SAL) was prepared from red pine (*Pinus densiflora* Sieb. et Zucc) by treating it with 72 wt% sulfuric acid in the usual manner.[12]

Phenolation of SAL

A mixture of 1.0 g SAL and 6.3 g phenol in 15 ml 72 wt% sulfuric acid was stirred at 60°C for 6 h. After quenching by dilution with 560 ml water, the suspension was boiled for 3 h as in the Klason determination of lignin. The solids were filtered out and washed with warm water (60°C) until the washing was neutral to give 1.15 g phenolized SAL (P-SAL).[3]

Mannich reaction of SAL and P-SAL

Lignin samples were reacted with formaldehyde and dimethylamine at 60°C under various reaction conditions (Tables 1, 2). After the reaction mixture was dialyzed with a cellulose tube (molecular weight cutoff was about 12 000) to remove excess reagents, the reaction products were lyophilized to yield the Mannich reaction products (M-SAL and MP-SAL).

Solubility of lignin samples

About 10 mg of each lignin sample was stirred in 1 ml of water at room temperature for 1 h. After centrifugation, the amount of undissolved residue was determined.

Table 1. Mannich reaction of **I** (0.2 mmol) with dimethylamine [$NH(CH_3)_2$] and formaldehyde (HCHO) in 1 ml dioxane at 50°C

Trial no.	Reaction conditions				Yield (%) of products **I–V**					
	$HN(CH_3)_2$ (mmol)	HCHO (mmol)	Time (h)	AcOH (ml)	**I**	**II**	**III**	**IV**	**V**	Total
1	0.22	0.22	0.5	0.2	62.9	18.2	10.1	1.5	0	92.7
2	0.44	0.44	0.5	0.2	39.5	20.3	19.3	7.3	0.6	87.0
3	1.10	1.10	0.5	0.2	9.7	11.8	25.7	22.2	6.7	76.1
4	2.20	2.20	0.5	0.2	0.7	1.6	13.8	26.7	24.2	67.0
5	1.10	1.10	0.5	0	35.0	19.4	22.2	9.3	0	85.9
6	1.10	1.10	2	0.2	0.3	0.5	4.6	13.8	43.0	62.2
7	1.10	1.10	4	0.2	0	0	1.4	5.5	53.0	59.9

Table 2. Mannich reaction of SAL (70 mg, 0.36 mmol)[a] and P-SAL (100 mg, 0.36 mmol)[b] in 10 ml 80% aqueous dioxane and 1 ml AcOH at 60°C

Trial	Reaction conditions				Product		
	Lignin	$HN(CH_3)_2$ (mmol)	HCHO (mmol)	Time (h)	Weight solubility (mg)	$CH_2N(CH_3)_2$ (no./C_9 or C_9-C_6)	
						Insoluble fraction	Total
1	SAL	3.96	3.96	4	68.1 (0%)	0.3[c]	0.3[c]
2	SAL	39.60	39.60	20	68.0 (0%)	0.4[c]	0.4[c]
3	P-SAL	0.72	0.72	4	97.6 (0.4%)	–	0.2[d]
4	P-SAL	1.98	1.98	4	97.5 (13.0%)	–	0.7[d]
5	P-SAL	3.96	3.96	4	97.5 (41.8%)	0.8[d]	0.9[d]
6	P-SAL	3.96	3.96	6	97.3 (100%)	–	1.0[d]
7	P-SAL	3.96	3.96	48	97.6 (100%)	–	1.3[d]

[a] Molecular weight of SAL was assumed to be 186/C_9[16]

[b] Molecular weight of SAL was assumed to be 275/C_9-C_6[3]

[c] Per C_9 unit

[d] Per C_9-C_6 unit

Measurement of surface tension

Surface tension measurements were performed at 25°C using a Kyowa Interface Science CBVP-Z instrument, based on the Wilhelmy technique. Commercial lignosulfonate (Vanillex N) and cationic surfactant (Arquad T-800; monoalkyltrimethylammonium chloride: C_{16}-C_{18}) (Nippon Paper Industries and Lion Corp., respectively) were used as comparative materials.

Spectrometry

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of compounds in deuterochloroform were recorded with TMS as an internal standard on a Jeol TNM-EX270 FT NMR spectrometer. The mass spectrometry (MS) spectra were recorded on a Jeol D-300 mass spectrometer.

Results and discussion

Mannich reaction of 1-guaiacyl-1-*p*-hydroxyphenylethane

The Mannich reaction occurs between a carbon with high electron density and an immonium ion ($CH_2 = N^+R_2$, where R is the alkyl group) formed from formaldehyde and an amine. Therefore, an aminomethyl group in the Mannich reaction can be introduced at the *ortho* position of a phenolic hydroxyl group in hydroxyphenyl nuclei or at the 5-position of guaiacyl nuclei (or both).[13,14] To elucidate the chemical reactivity of *p*-hydroxyphenyl and guaiacyl units in phenolized sulfuric lignin toward a Mannich reaction, 1-guaiacyl-1-*p*-hydroxyphenylethane (**I**) as a simple phenolized sulfuric acid lignin model compound was reacted with dimethylamine and formaldehyde. The Mannich reaction had been applied for kraft lignin to obtain the ion-exchange resin.[15]

Four compounds (**II–V**) were isolated from the Mannich reaction products of **I** by silica-gel column chromatography. In the ^{13}C-NMR spectrum of **II**, the intense characteristic signals near 115 and 129 ppm due to the *p*-hydroxyphenyl nucleus disappeared, suggesting introduction of an aminomethyl group into the *p*-hydroxyphenyl nucleus. A methylene carbon signal and an $—N(CH_3)_2$ carbon signal appeared at 63.1 and 44.6 ppm, respectively. Mass and ^{1}H-NMR spectra indicate that **II** has the structure shown in Fig. 1. In the ^{13}C-NMR spectrum of **III**, two intense signals of 115.4 and 128.6 ppm due to the *p*-hydroxyphenyl nucleus, 10 aromatic carbon signals, and signals at 62.5 and 44.5 ppm due to methylene and $—N(CH_3)_2$ carbons, respectively, together with mass and ^{1}H-NMR spectra suggest that **III** has one aminomethyl group in the guaiacyl group. In the mass spectrum of **IV**, a molecular ion peak at *m/z* 358 indicates the introduction of two aminomethyl groups into the aro-

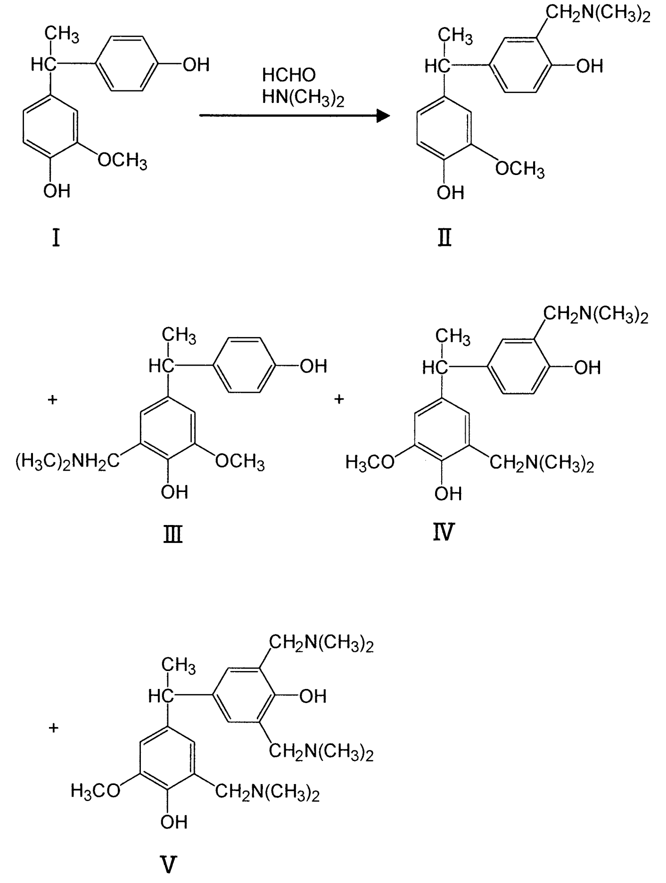

Fig. 1. Mannich reaction of model compound **I**

matic nuclei. A detailed analysis of five aromatic proton signals in the ^1H-NMR spectrum together with the absence of strong signals due to the *p*-hydroxyphenyl nucleus in the ^{13}C-NMR spectrum confirmed that **IV** has one aminomethyl group each in the *p*-hydroxyphenyl and guaiacyl nuclei, as shown in Fig. 1. The molecular ion peak of **V** at *m/z* 415 indicates the introduction of three aminomethyl groups. Spectroscopic analysis suggests that the compound has the structure shown in Fig. 1. The intensive signal at 128.0 ppm in the ^{13}C-NMR spectrum and a singlet at 6.84 ppm in the ^1H-NMR spectrum of **V** confirmed the structure.

The yields of Mannich reaction products **II–IV**, which were determined by gas chromatography, are summarized in Table 1. When equal amounts of reactants were used (trial 1), the yield of **II** was higher than that of **III**, indicating slightly higher reactivity of the *p*-hydroxyphenyl nucleus. This phenomenon was different from the hydroxymethylation[11] of **I** with formaldehyde in an alkaline medium because the guaiacyl nucleus had a higher reactivity. Addition of a small amount of acetic acid (AcOH) promoted the Mannich reaction (trials 3 and 5). As could can be expected, the increased mole quantities of the reagents (trials 1–4) and the prolonged reaction time (trials 3, 6, 7) brought about an increase in the aminomethyl group and finally yielded a fully substituted product (**V**). The total yields of reaction products were decreased when the reaction progressed. Thin-layer chromatography analysis revealed that some compounds remained at the starting point. We could not analyze these compounds in this study, but the result suggested that the condensation reaction occurred during the Mannich reaction.

Mannich reaction of SAL and P-SAL

The reaction conditions and experimental results of the Mannich reaction of SAL and P-SAL are summarized in Table 2. The solubility of dimethylaminomethylated products (M-SAL and MP-SAL) is the same as that in water. The content of the dimethylaminomethyl group was calculated based on the assumption that all of the nitrogen determined by elementary analysis is attributed to the dimethylaminomethyl groups. On the basis of the results from the model compound, 11 equivalents of reaction reagents were used to introduce dimethylaminomethyl groups to SAL itself (trial 1), but the number of the dimethylaminomethyl groups was $0.3/C_9$ when the reaction time was 4 h. The number of dimethylaminomethyl groups of M-SAL was only $0.4/C_9$, and the yielded M-SAL could not dissolve in water, even when the amounts of the reagents were increased and the reaction time was prolonged (trial 2). Previous investigation[16] showed that the content of phenolic hydroxyl groups of softwood SAL is 1.8 times higher than that of corresponding milled wood lignin (MWL). Based on the assumption that the number of phenolic hydroxyl groups of softwood MWL was 0.27/OMe,[17] softwood SAL has a phenolic hydroxyl group value of 0.49/OMe. The introduction of 0.4 dimethylaminomethyl group/C_9 to the SAL means that the Mannich reaction occurs at about 80% *ortho* position of the phenolic hydroxyl groups in the SAL. Thus, the insolubility of the M-SAL suggests that the introduction of 0.4 dimethylaminomethyl group/C_9 to SAL is insufficient to prepare a soluble cationic surfactant.

In a previous experiment[3] it was found that phenolation of SAL in the presence of 72% sulfuric acid as a catalyst brings about the selective substitution of condensed-type aromatic nuclei formed during sulfuric acid treatment of softwood lignin to the *p*-hydroxyphenyl nucleus. The P-SAL has almost the same molecular weight as MWL.[3] P-SAL with *p*-hydroxyphenyl nuclei at the benzylic position of the lignin side chain[3] might have much higher reactivity than SAL. In this experiment, P-SAL with one *p*-hydroxyphenyl group per phenylpropane unit was prepared by phenolation of SAL in the presence of a sulfuric acid catalyst. Recently, lignin-based polymers[18] have been prepared by treating woody materials with water-insoluble phenols such as cresol in 72% sulfuric acid solution. P-SAL is estimated to have the structure similar to that of a polymer prepared from woody materials and water-soluble phenol instead of the water-insoluble phenols used in the above method. As shown in Table 2, although the number ($0.2/C_9$-C_6) of dimethylaminomethyl groups was less than that in the insoluble M-SAL, the MP-SAL was slightly dissolved in water (trial 3), suggesting that the molecular weight of P-SAL is lower than that of SAL. When the amount of the

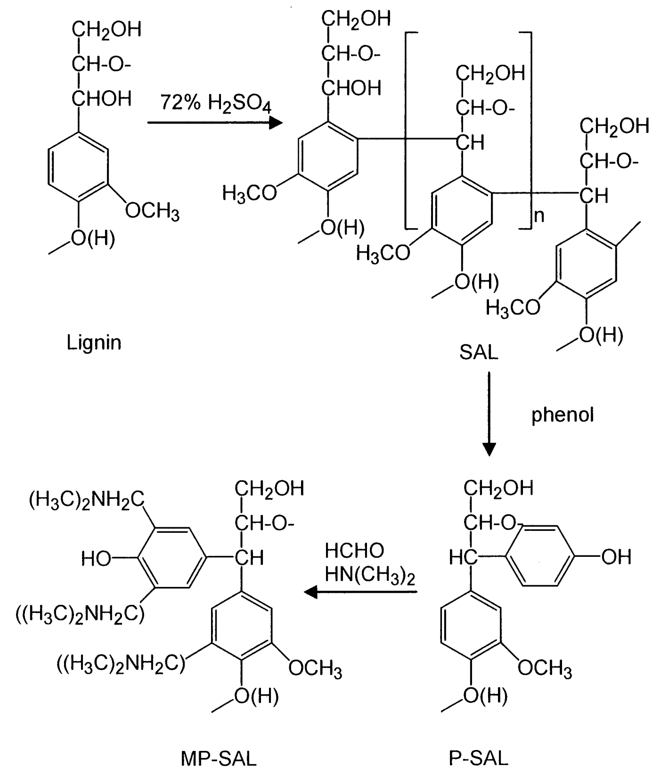

Fig. 2. Conversion of lignin to water-soluble cationic surfactant (MP-SAL)

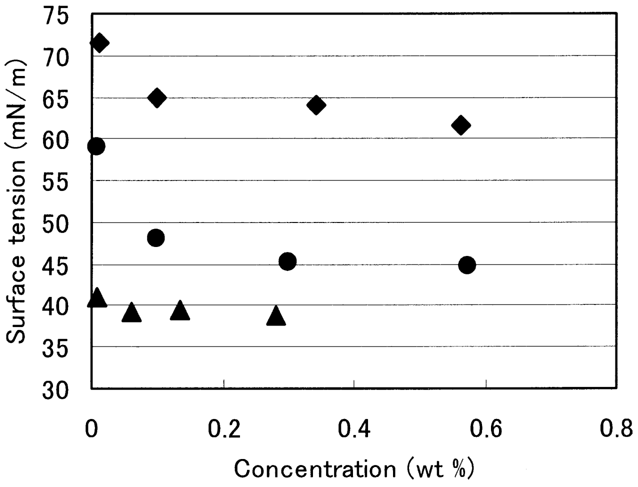

Fig. 3. Plots of surface tension versus concentration of MP-SAL (*circles*) and commercial surfactants [Vanillex N (*diamonds*) and Arquad T-800 (*triangles*)]

reaction reagents was increased (trials 3–5), the number of introduced dimethylaminomethyl groups was increased and the solubility reached about 40% (trial 5). The prolonged reaction time brought about an increase in the number of dimethylaminomethyl groups (trials 5–7). Finally, a soluble cationic surfactant (trial 7) with 1.3 dimethylaminomethyl units per C_9-C_6 could be prepared in a quantitative yield from P-SAL. As can be seen from Table 2, introduction (trial 6) of 1.0 dimethylaminomethyl group per C_9-C_6 unit into P-SAL is necessary to prepare the water-soluble cationic surfactant.

Solubilities of 41.8% and 100% when the numbers of introduced dimethylaminomethyl groups were 0.9/C_9-C_6 and 1.0/C_9-C_6, respectively, revealed that the amount of the introduced dimethylaminomethyl group significantly affected the solubility of MP-SAL in water. In regard to the solubility of polymers, it is often seen that the hydrophilic group acts on the solubility to a large extent. The acetyl group content plays an important role in the deacetylation of chitin[19] in terms of water solubility. Chitin is solubilized completely when the degree of deacetylation is about 50%, but the solubility is decreased when the degree of deacetylation is lower or higher than 50%. In previous research[4] it was also shown that the sulfonate group introduced to hydroxymethylated P-SAL sensitively affected its solubility. Thus it seems that hydrophilic groups act sensitively on the solubility of P-SAL.

This study reveals a possible route for the chemical conversion of acid hydrolysis lignin with highly condensed structures into a novel soluble cationic surfactant. The tentative structure and the synthetic route of MP-SAL are shown in Fig. 2. The reaction sequence comprises a nucleophilic attack of the *ortho* positions of phenolic hydroxyl units on the immonium ion $[CH_2{=}N^+(CH_3)_2]$.

Characteristics of MP-SAL as a surfactant

To characterize MP-SAL as a surfactant, surface tension was measured. Figure 3 shows plots of surface tension versus the concentration (at 25°C) of prepared MP-SAL with 1.3 dimethylaminomethyl group/C_9-C_6 (trial 7 in Table 2) and commercial surfactants. The surface tension was decreased to 45 mN/m, and the degree of the decrease was less than that of monoalkyltrimethylammonium chloride (a commercial cationic surfactant) but much larger than that of lignosulfonate (a commercial surfactant from lignin). Thus MP-SAL has high surface activity. Other capabilities of MP-SAL as a surfactant require further study.

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