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Modification of lignin with dodecyl glycidyl ether and chlorosulfonic acid for preparation of anionic surfactant

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Abstract Lignin was modified through incorporation of lipophilic and hydrophilic groups for the preparation of surfactant. In this case, alkaline lignin reacted with dodecyl glycidyl ether in the presence of dimethyl benzyl amine to incorporate lipophilic long alkyl chains, and then sulfonated with chlorosulfonic acid for the introduction of hydrophilic sulfonic acid group. Results showed that the reaction between dodecyl glycidyl ether and carboxy group in lignin was the predominant reaction at 95 °C-110 °C. It was found that the surface tension of the synthesized lignin surfactant solution was lower than that of commercial surfactant sodium dodecylbenzenesulphonate when concentration was below 0.4 %, indicating that the surfactant prepared from alkaline lignin had a good surface activity. A lowest critical micelle concentration of 0.50 g L^{-1} and the corresponding surface tension at 29.17 mN/m were achieved when the surfactant was derived from the lignin grafted with dodecyl glycidyl ether at 110 ºC. The anionic lignin surfactants prepared in this study is a promising feedstock as detergents or to enhance oil recovery.

1. Introduction

The use of sustainable resources for energy and advanced eco-friendly material has drawn much attention due to the increased consumption of fossil resources associated with energy crisis and climate change.[1, 2] Lignocellulose, mainly composed of cellulose, hemicellulose and lignin, is a promising and renewable resource for biofuel, chemicals, and biomaterials without competition with human's food.[3] There are some conundrums of the development of bio-ethanol for making biomass-to-biofuels economic[4], but it has great potential economic benefits to develop new materials and chemicals derived from lignocellulose. After cellulose and hemicelluloses, lignin is the third most abundant biopolymer from biomass and considered as the most abundant aromatic renewable resource. Lignin mainly consists of *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units derived from three major monolignols, namely, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These units are connected by various inter-unit linkages (e.g., *β*-*O*-4′, *β*-5′, *β*-*β*′, 5-5′, 5-*O*-4′, and *β*-1′, etc.) through an enzyme-initiated dehydrogenative polymerization [5, 6] Lignin can be isolated from wood, annual plants (such as wheat straw) and agricultural residues (such as corncobs) by different processes.[7, 8] However, lignin is considered as low-value and underutilized by-product from pulping and bio-refinery industries. Most of lignin fraction resulted from these processes is burned as fuel, and only a small portion of lignin is converted to commercial products. The effective utilization of lignin to produce value-added products through chemical modification will make the biomass industry economically feasible with respect to the replacement of chemicals and materials derived from fossil sources. Lignin is an excellent candidate for chemical reactions due to its highly functional characteristics (rich in phenolic and aliphatic hydroxyl groups) for the development of new chemicals.

Surfactants are extremely important chemicals, and numberless types of surfactants are used for a myriad of applications, thus the development of lignin surfactant has a good industrial prospect. Lignin itself is not very useful as a surfactant because of the nature character of lignin, for example, the complex macromolecular structure, the large molecular weight, the low hydrophilicity and lipophilicity.[9, 10] To work effectively, most surfactant require water soluble and oil soluble characteristics. Lignin must be changed into the fraction which has the hydrophilic or amphiphilic property. To date, the introduction of hydrophilic groups into lignin by sulfonation[11, 12], carboxylation[13, 14], and Mannich reaction[15] has been investigated by many researchers. However, these methods can only enhance hydrophilicity but to lipophilicity of lignin, and the surface activity of these lignin surfactants is not satisfactory. In fact, a good lignin surfactant requires water soluble and oil soluble characteristics by the incorporation of both lipophilic and hydrophilic groups. *Morrow et al.* [16] have described a method of producing surfactants for enhancing oil recovery from lignin by two reactions of lignin, i.e., alkylation with different alkyl halides at phenolic sites, sufficient oxidation to break the lignin into smaller polymeric and monomeric units, and sulfonation to increase their water solubility. *Naae et al.* [17] reduced lignin in the presence of CO and H_2, the resulted products were alkoxylated with α–olefin epoxide introducing a long alkyl chian, and these compounds were changed into oil soluble lignin surfactant by sulfonation, sulfation and alkoxysulfation. *Zeng et al.* [18] have reported that hydrophilic sulfonic group and lipophilic adbietic group were introduced into the molecular structure of Kraft lignin, and the rosin-modified lignosulfonate lowed the surface tension of a 10 g L^{-1} aqueous solution to 49.3 mN/m.

The aim of the present study was to prepare lignin surfactant by simultaneous incorporation of lipophilic and hydrophilic groups into lignin. Alkaline lignin was modified with dodecyl glycidyl ether in the presence of dimethyl benzyl amine as a catalyst, and then was converted into anionic surfantant by sulfonation with chlorosulfonic acid. The structure of lignin after reaction with dodecyl glycidyl ether was examined by FT-IR, GPC, ^{31}P-NMR and ^{13}C-NMR, and the surface activity of the lignin surfactant was investigated through determining the surface tension of the aqueous solution.

2. Experimental

2.1. Materials

Alkaline lignin (AL) from corncob was obtained from Shandong Longlive Bio-technology Co., Ltd, China. Laurylalcohol, epichlorohydrin (ECH), tetrabutyl ammonium bromide (TBAB), N,N-dimthylbenzylamine (BDMA), sodium dodecyl benzene sulfonate (SDBS) and dimethyl sulfoxide (DMSO) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd, China. Chlorosulfonic acid (99%) was provided by Xiya reagent (Chengdu, China).

2.2. Preparation of dodecyl glycidyl ether (DGE)

To a vigorously stirred mixture containing 37.2 g（0.2 mol）of laurylalcohol, 200 mL of toluene, 50.0 g of 48% aqueous sodium hydroxide solution and 3.2 g (0.01 mol) of TBAB, 37.0 g（0.4 mol）of ECH were added dropwise for 15 min at ambient temperature, and the reaction was run for 6 h at 50 °C. When the resulting solution was cooled to room temperature, the organic layer was separated and washed 4 times with distilled water (200 mL, 60 °C). Then the organic layer was evaporated at 60 °C under reduced pressure to obtain DGE. The epoxy value of DGE was 0.33 mol epoxy / 100 g DGE, determined according to the method described by Hou.[19]

2.3. Reaction of AL with DGE

A 250 mL round-bottom flask containing 8.0 g lignin, 1.8 g BDMA, 8.0 g DGE and 160 mL DMSO was heated for 5.0 h at various temperatures (95-110 °C). The reaction was quenched by adding 20 mL of 2.0 M HCl under stirring for 30 min at room temperature. The solvent was removed by rotary evaporation, and the residue was washed with distilled water and petroleum ether for several times, and then dried overnight at 60 °C to give grafted lignin, named as DGE-AL.

2.4. Sulfonation of DGE-AL

The sulfonation of DGE-AL was conducted according to the procedure in a previous report with minor modifications.[11] A total of 2.0 g chlorosulfonic acid in 20 mL anhydrous dichloromethane (CH_2Cl_2) was added dropwise into 1.0 g of DGE-AL in 10 mL dichloromethane. The mixture was mechanically stirred for 2 h in an ice bath. Next, 30 mL of 2 M NaOH was added and the mixture was stirred for 1 h in an ice bath, and then it was adjusted with 1 M HCl to pH 8.0. The resulting mixture was dialyzed with a cellulose tube (cut off Mw-3000) against water and lyophilized to yield sulfonated DGE-AL, named as SD-AL.

2.5. Sample characterization

FT-IR spectra were recorded in a Thermo Scientific Nicolet iN10 FT-IR Microscope (Thermo Nicolet Corporation, Madison, WI, USA) equipped with a liquid nitrogen cooled MCT detector. The spectra were collected in the range of 4000-650 cm^{-1} at 4 cm^{-1} resolution. NMR spectra were recorded on a Bruker AVIII 400 MHz spectrometer at 25 ºC. For ^{13}C-NMR spectra, 80 mg samples were dissolved in 1 mL of DMSO-d_6. The sample was modified following the procedure below for ^{31}P-NMR determination. Approximate 30 mg of oven-dried sample was dissolved in pyridine/chloroform (1.6:1, v/v) in a small vial and stirred continuously. N-hydroxyl naphthalimide was used as internal standard, and chromium acetylacetonate as the relaxation reagent. Then, 2-chlorl-4,4,5,5-tetramethyl-1,3,2-dioxa-phosphalane (TMDP) was used for phosphitylation of hydroxyl groups. The molecular weight of the sample was determined by gel permeation chromatography (GPC). The lignin sample was dissolved in tetrahydrofuran (2 mg/mL), and then the solution was analyzed on a high performance liquid chromatography system (Agilent 1200 series, Agilent technologies, USA) with a DAD detector. The molecular weights were calibrated via monodisperse polystyrene standards. The sulfur content of the lignin surfactant was examined by elemental analysis using a Vario EL III Elemental analyzer instrument (Elementar, Germany) according to a previous report.[20]

2.6. Measurement of surface tension

An automatic surface tensiometer (JK99B, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd) was used to measure the surface tension of the surfactant solution at different concentrations at room temperature (18 °C). Deionized water (surface tension 74.950 mN/m) was employed for reference, and commercial surfactant SDBS was used as a control. Critical micelle concentration (CMC) values of lignin surfactants were identified from the plot of the surface tension versus the surfactant concentration of water solution.

3. Results and discussion

3.1. Synthesis and characterization of DGE-AL

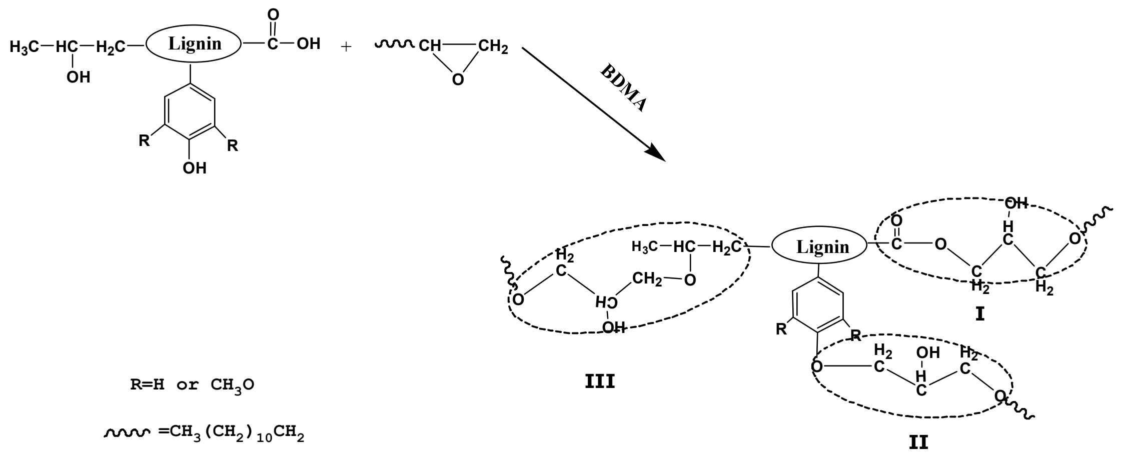
Typically, Lewis bases are used to accelerate the reaction between epoxides and the hydroxyls of phenols, alcohols and carboxyl.[21] In this study, BDMA was chosen as a catalyst of the reaction between DGE and lignin, and DGE was introduced into lignin through lignin hydroxyl-epoxide reaction (see Scheme 1). Because of the low hydrophilicity and lipophilicity, lignin had a low solubility in neutral water and most of organic solvents. For a homogeneous reaction between lignin and DGE, DMSO was employed as a solvent for the reaction system. In order to avoid self-polymerization of DGE in the presence of tertiary amine[22], the reaction temperature was set at 95, 100 and 110 °C. After reaction, hydrochloric acid was used to deactivate the remnant DGE, and the inactivated DGE and DGE homopolymer were washed off with petroleum ether. As seen from Table 1, the DGE-AL yields were as high as 62.68-65.25%, and the molecular weights of the products derived from the reaction conducted at 95, 100, and 110 °C were 1300, 1410, and 2050 g mol^{-1} , respectively.

Table 1 The yields, weight average (M_w) and number average (M_n) molecular weight of the products from the reaction of DGE with alkaline lignin

Samples [a]	Yield (%) [b]	M_w (g mol^{-1})	M_n (g mol^{-1})	M_w/M_n
DGE-AL 1	65.25	2050	720	2.85
DGE-AL 2	64.31	1410	600	2.37
DGE-AL 3	62.68	1300	580	2.23
AL	-	850	540	1.59

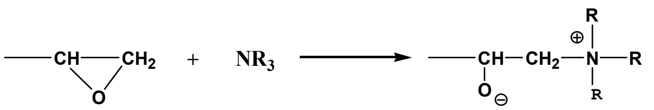
[a] AL, raw material alkaline lignin; DGE-AL 1, DGE-AL 2 and DGE-AL 3 were obtained by the reaction of DGE with lignin in the presence of BDMA at 110, 100 and 95 °C for 5 h, respectively.

[b] the yield of DGE-AL was based on the total weight of reactant.



Scheme 1 The reaction of DGE with lignin in the presence of BDMA.

^{31}P-NMR technique has been widely applied in classification and quantitative determination of several different classes of hydroxyl groups in the native and modified lignin.[23-25] In this study, phosphitylating agent TMDP was utilized to obtain the qualitative and quantitative information about hydroxyl groups in lignin before and after graft. The ^{31}P-NMR spectra of the samples are illustrated in Figure 1 and the contents of different hydroxyl groups are listed in Table 2. For DGE-AL 1 and DGE-AL 3, the content of total OH was lower than that of AL, indicating the successful introduction of DGE into lignin in the presence of BDMA. As compared to DGE-AL 3, the dramatic reduction of the carboxylic OH content in DGE-AL 1 suggested that the reaction between epoxide and carboxyl was the predominant reaction when reaction temperature increased from 95 °C to 110 °C. This can be explained by the mechanism of glycidyl ether reactions with alcohols, phenols and carboxylic acids in the presence of tertiary amine as a catalyst.


(1)

Z

From Equation 1, a zwitterion (Z) was formed by the interaction between tertiary amine and epoxide which acted as an efficient catalyst due to its high basicity.[21] Because of the relatively high acidity of carboxyl in lignin, the reaction between carboxyl and glycidyl ether occurred first. As see from Fig. 1, the chemical shifts of 150.0-145.4 ppm, 144.5-137.0 ppm, and 136.0-133.6 ppm are assigned to aliphatic, phenolic, and carboxylic acid OH, respectively.[26] With respect to the reaction mechanism of hydroxyl-glycidyl ether reactions, the following hypothesis was made: some new hydroxyl groups were derived from the open-ring reaction of epoxy group of DGE. Accordingly, three new kinds of signals were assigned at the chemical shifts of aliphatic OH, derived from the reactions of DGE with aliphatic, phenolic, and carboxylic acid OH in lignin. This was supported by the presence of three new peaks (147.9-147.4, 147.1-146.8, and 146.6-145.8 ppm) in the spectra of DGE-AL 1 and DGE-AL 3, which correspond to the chemical shifts of aliphatic OH. From Fig. 1, the signals at 146.6-145.8 ppm varied more noticeably as compared to those at 147.9-147.4 ppm and 147.1-146.8 ppm probably due to the large reduction of the content of carboxylic OH in DGE-AL 1 as compared to DGE-AL 3 (Table 2). The signals at 146.6-145.8 ppm were probably due to the hydroxyls derived from carboxyl-glycidyl ether reaction, whereas the absorptions at 147.9-147.4 ppm and 147.1-146.8 ppm probably correspond to the hydroxyl groups derived from the alcohol and phenol-glycidyl ether reactions, respectively.

Table 2 Quantification of hydroxyl content of alkaline lignin before and after reaction with DGE by quantitative ^{31}P-NMR method

Samples [a]	Hydroxyl content (mmol g^{-1} of lignin)						
	Aliphatic OH	Syringyl OH	Guaiacyl OH	*p*-Hydroxy phenyl OH	Carbox ylic OH	Total phenol OH	Total OH
AL	2.26	0.84	1.67	1.02	2.24	1.52	8.03
DGE-AL 1	2.77	0.64	1.16	0.55	0.39	1.04	5.51
DGE-AL 3	2.70	0.78	1.32	0.40	0.88	1.20	6.27

[a] AL, DGE-AL 1 and DGE-AL 3 corresponding to the lignin samples in Table 1.

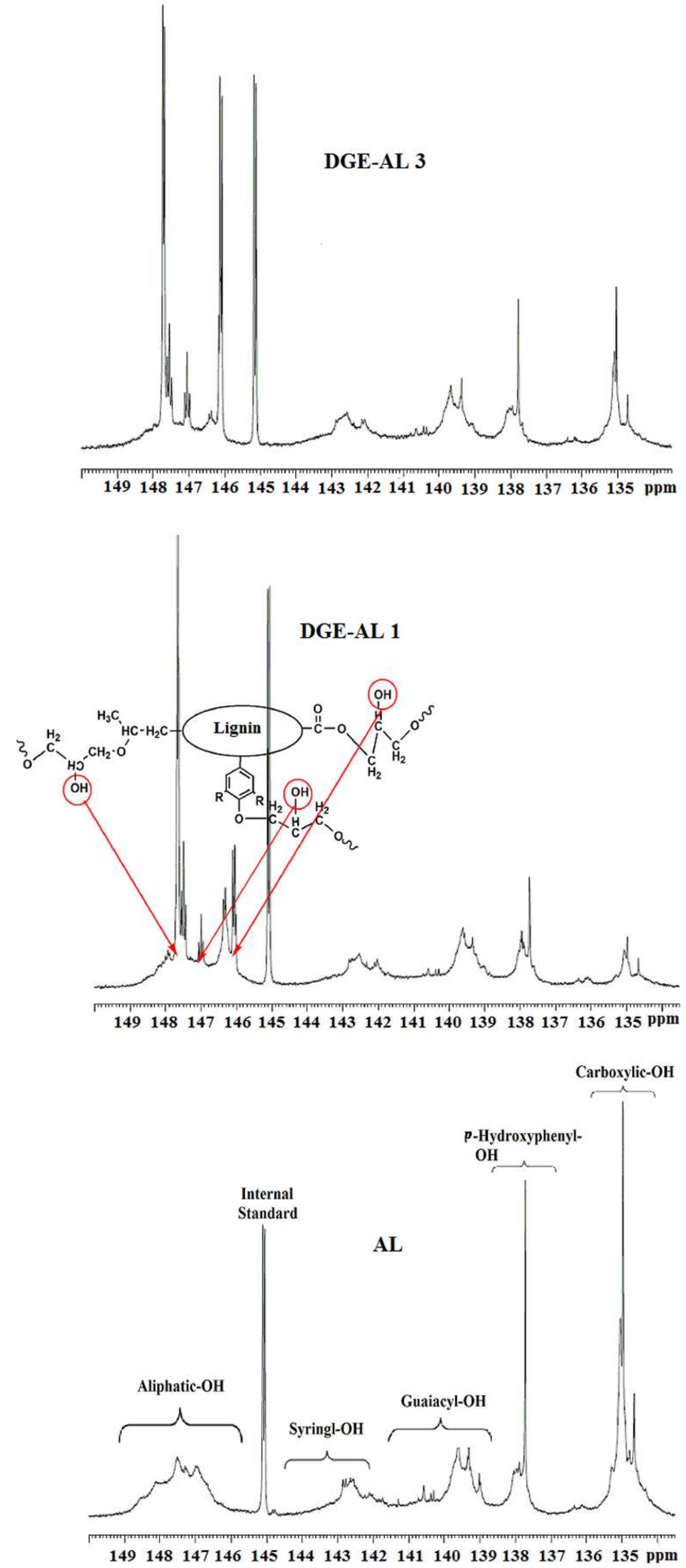


Fig. 1 ^{31}P-NMR of AL, DGE-AL 1 and DGE-AL 3.

More information of the structure of DGE-AL was acquired by FT-IR and ^{13}C-NMR spectra. Fig. 2 shows the FT-IR spectra of the samples. As compared to AL, the intensity of the absorption bands at 2924 and 2853 cm^{-1} (saturated C-H stretching vibration) increased, the absorption at 1120 cm^{-1} corresponding to C-O-C stretching vibration became clearer, and a new peak appeared at 731 cm^{-1} ($(CH_2)_n \geq 2$ rocking vibration) in DGE-AL spectra. The results above suggested that long alkyl chain was introduced into lignin through the reaction between DGE and lignin in the presence of BDMA, in accordance with the result of ^{31}P-NMR analysis aforementioned.

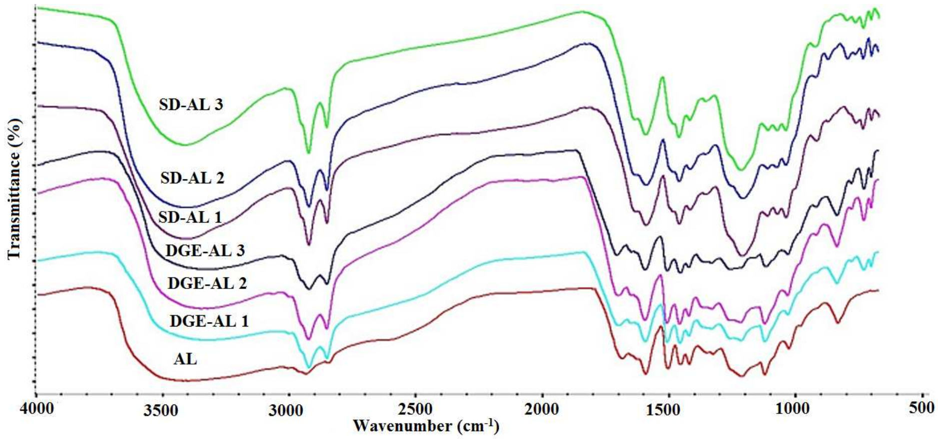


Fig. 2 FT-IR spectra of AL, DGE-AL and SD-AL samples.

Fig. 3 shows the ^{13}C-NMR spectra of AL and DGE-AL. In the aliphatic region, five well-defined peaks were observed at 14.0, 25.6, 28.7, 29.0 and 31.3 ppm in DGE-AL spectra, and these peaks are assigned to the methyl carbon and methylene carbon of dodecyl chains. Generally, the ^{13}C-NMR chemical shift of the carbon atoms bonded to oxygen (CH_2O, C-O-C, C-O-C=O) in glycerol ether or glycerides are assigned at the bands of 60.0-70.0 ppm.[23-29] As expected, the additional peaks at 60.0-72.7 ppm attributed to the carbon atoms in glycerol ethers cross-linked structure (see Scheme 1, I, II, III) were observed in DGE-AL spectra. Because of the complexity of the ring-opening reaction of epoxy compound as well as the complicated structure of lignin macromolecule,[30] no effort was made to assign these peaks. It was concluded that the expected compounds were formed in the reaction of lignin and DGE under the catalysis of dimethylbenzylamine.

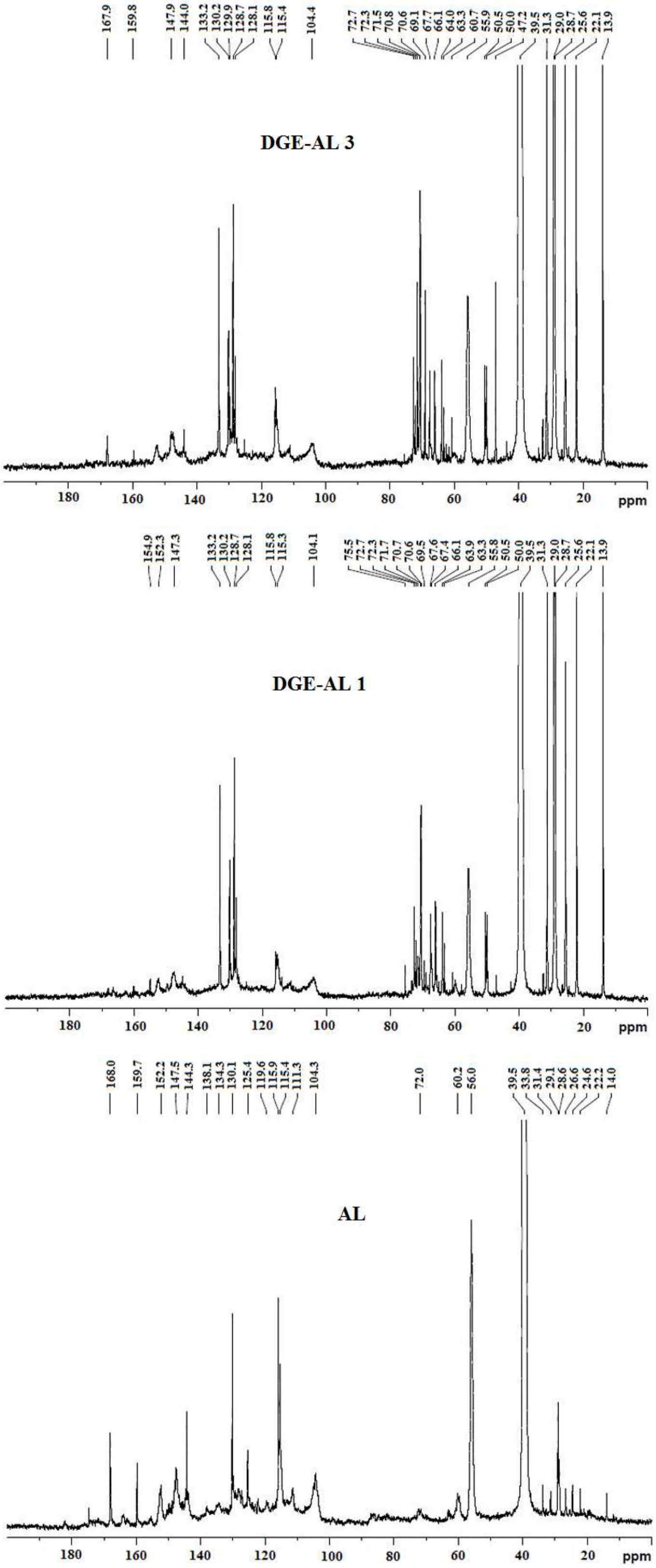


Fig. 3 ^{13}C-NMR of AL, DGE-AL 1 and DGE-AL 3.

3.2. Preparation and characterization of SD-AL

Surfactants are amphiphilic materials containing both a polar long-chain hydrocarbon "tail" and polar, usually ionic, "head" groups. Because of the lack of hydrophilic groups, only the introduction of long alkyl chain into lignin cannot make lignin became a good surfactant. In this case, lignin achieved both hydrophilic and hydrophobic characteristics which were different from those of commercial surfactants. AL grafted with DGE under different temperatures were sulfonated with chlorosulfonic acid, and then neutralized with sodium hydroxide, yielding anionic surfactant SD-AL. The FT-IR spectra of SD-AL are shown in Fig. 2. For the spectra of SD-AL, the intensity of the bands at 2924 and 2853 cm^{-1} correspond to methyl and methylene vibration, respectively. The new absorptions at 1073 and 1040 cm^{-1} correspond to the symmetric and asymmetric stretching vibrations of S–O bond, respectively.[31] The appearance of a strong peak at 1217 cm^{-1} is indicative of the S=O stretch of the sulfatesalt as well as the sulfonic acid,[32] indicating the existence of SO_3 groups in SD-AL. As compared to DGE-AL, the intensity of the peak at 1120 cm^{-1} corresponding to C-O-C stretching vibration in SD-AL became weak, indicating the partial hydrolysis of ester groups during the preparation of SD-AL.

The effect of hydrolysis of ester groups during the preparation of SD-AL was investigated through examining the content of the dichloromethane-insoluble components of DGE-AL after treatment with 2 M NaOH for 1 h in an ice bath. Briefly, 1g of DGE-AL was added to 30 mL of 2 M NaOH and the solution was stirred for 1h in an ice bath. After the reaction, DGE-AL was regenerated by precipitation through adjusting the resulting solution to pH=2 with 30% acetic acid. The result showed that the contents of dichloromethane-insoluble components were 29.71%, 27.72 % and 26.43% of the weight of regenerated DGE-AL 1, DGE-AL 2 and DGE-AL 3, respectively. This indicated that some de-alkylation of DGE-AL occurred during the preparation of SD-AL. The generation of dichloromethane-insoluble components should be due to the hydrolysis of the ester groups in DGE-AL. Thus, optimization of the neutral condition for sulfonic acid group should be conducted in a future study.

Table 3 Elemental analysis, yield, CMC and surface tension of water at CMC of all surfactant samples

Samples [a]	Elemental analysis (%)			Yield (%) [b]	CMC (g L^{-1})	Surface tension of CMC (mN/m)
	S	C	H			
AL	-	63.00	5.60	-	-	-
SD-AL 1	7.14	45.00	5.21	78.2	0.50	29.17
SD-AL 2	7.27	46.15	5.96	77.8	0.55	29.65
SD-AL 3	7.81	46.23	5.91	78.5	0.58	30.21
SDBS	-	-	-	-	0.97	30.50

[a] SDBS, commercial surfactant sodium dodecyl benzene sulfonate; SD-AL 1, SD-AL 2 and SD-AL 3 derived from the sulfonation of DGE-AL 1 DGE-AL 2, and DGE-AL 3 at the same condition, respectively.

[b] the yield of SD-AL was based on the weight of DGE-AL.

-, no measurement.

3.3. Characteristics of SD-AL as a surfactant

Fig. 4 shows the isotherms of the surface tension of aqueous solution plotted against concentrations of SD-AL as compared to commercial surfactant SDBS. By the addition of lignin surfactant, the surface tension of water decreased with the increase of the concentration. For SD-AL 1, SD-AL 2, and SD-AL 3, the surface tension was lower than that of SDBS when the concentration of aqueous surfactant solution was below 0.4 %. After sulfurization under the same conditions, the lignin surfactant derived from the reaction of lignin with DGE at a high temperature had a low surface tension at equivalent concentration of aqueous solution. It was consistent with the result reported by Košíková *et al.*, in which the higher amount of alkylhalide was used to modify the prehydrolysis lignin, the lower surface tension was observed.[33]

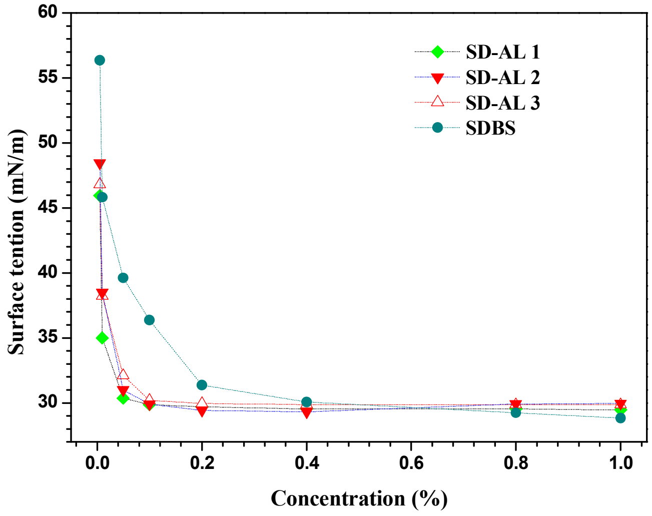


Fig. 4 Isotherms of surface tension of water plotted against concentration of SD-AL surfactant and SDBS.

Generally, the concentration of surfactant influences the physical and chemical properties of surfactant solution. CMC is considered to be a fundamental property of surfactants. A number of interfacial phenomena such as detergency can take place due to the presence of micelles in solutions. In addition, other phenomena such as the surface tension reduction is not directly influenced by the formation of micelles.[34] Therefore, CMC and the corresponding surface tension are important indicators to measure the surface activity of surfactants SD-AL. As seen from the data listed in Table 3, the CMC of SD-AL decreased with the increase of reaction temperature between DGE and lignin, a lowest CMC (0.50 g L^{-1}) and the corresponding surface tension (29.17 mN/m) were achieved when the surfactant derived from the lignin grafted with DGE under 110 ºC. This was because under a similar content of sulfur, surfactant derived from the lignin grafted with DGE under high temperature has a high lipophilicity than that prepared under low temperature. The CMC and surface tension at the corresponding CMC of all surfactants derived from lignin were lower than the CMC (0.97 g L^{-1}) and the corresponding surface tension (30.50 mN/m) of the commercial surfactant SDBS, indicating that SD-AL surfactants had a good surface activity. Furthermore, the lignin surfactant prepared showed a good ability to reduce the surface tension of aqueous solution, comparable to those of the products prepared previously. In Košíková B's work,[33] a series of lignin-based surface active agents derived from alkylation of beechwood prehydrolysis lignin with laurybromide decreased the surface tension of aqueous solution to 30-40 mN/m at the concentration of 1 g L^{-1}. Homma *et al.*[35] reported that nonionic polymeric surfactants derived from the modification of acetic acid lignin with polyethylene glycol diglycidylethers lowed the surface tension of aqueous solution to 36 mN/m at the corresponding CMC (50g L^{-1}). The results of the present study suggested that lignin surfactants with high surface activity was prepared by modification of lignin with DGE and chlorosulfonic acid.

4. Conclusion

A long alkyl chain was successfully introduced into lignin by the reaction between lignin and DGE in the presence of BDMA as a catalyst. The reaction between DGE and carboxy group was the predominant reaction at 95 °C-110 °C. The surface tension of the lignin surfactant solution was lower than that of commercial surfactant sodium dodecylbenzenesulphonate when the concentration of surfactant solution was below 0.4 %, indicating that the surfactants prepared from modified alkaline lignin had a good surface activity. A lowest CMC (0.50 g L^{-1}) and the corresponding surface tension (29.17 mN/m) were achieved when the surfactant was derived from the lignin grafted with DGE at 110 ºC. The anionic lignin surfactants prepared in this study could be utilized as detergents or to enhance oil recovery.

Acknowledgements

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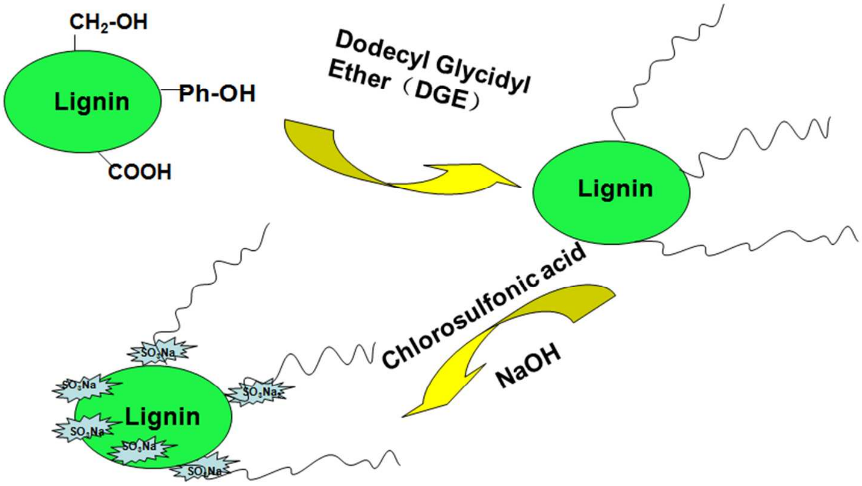

Improving the surface activity of lignin through chemical modification for preparation of anionic surfactant.