Electro-Degradation of Sodium Lignosulfonate

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ABSTRACT

The electro-degradation of sodium lignosulfonate was conducted in an electrolytic cell equipped with PbO_2 membrane electrode as the anode and stainless steel gauze as the cathode. Sodium lignosulfonate was degraded into substances with relatively low molecular weights. Some high molecular weight fractions were also formed during the reaction demonstrating that the condensation occurred simultaneously with degradation. The distribution and the characteristics of the products were greatly affected by the voltage, the electricity consumption, the current density, and the pH. Degraded lignosulfonate gave much lower surface tension and oil–water interfacial tension than unreacted lignosulfonate did in aqueous solution.

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INTRODUCTION

Lignosulfonate, obtained from the sulfite pulping process as a by-product produced in great amounts, is frequently used as a dispersant, emulsifier, tanning agent and slow-release fertilizer.[1,2] The utilization of lignosulfonate, however, is limited because the products manufactured from it seldom perform as well as those prepared from petrochemicals. The performance of lignosulfonates can be improved by chemical modification,[3–5] but the modification usually produces a complicated mixture and the isolation of the target products from the mixture is usually a complicated procedure. Therefore a method to utilize the modified lignosulfonate directly is preferred.

Conversion of lignosulfonates into low molecular substances is probably an effective way to increase their utility. Lignins have been successfully degraded into phenols, low molecular weight acids, and flammable gases and the degradation products can be used either as fuels, chemical products, or feedstock in the manufacture of polymeric materials.[6,7] The drawback of thermochemical liquefaction is that it must be conducted at elevated temperature and high pressure. Oxidation of lignin using nitrobenzene, metal oxides, and molecular oxygen in alkaline solution, peracetic acid, or other chemicals also gives products with low molecular weights.[8] The use of these oxidizing agents, however, presents problems such as toxicity, high price, and the potential for over-oxidation. Furthermore, such methods usually suffer from serious side reactions.

Electro-degradation is a potentially effective way to convert lignin into valuable organic chemicals. It not only modifies lignin molecules by cleavage of the side chain to increase the $-OH$ and $-COOH$ content, but more importantly it cleaves the lignin at ambient temperature.[9,10] Parpot et al.[11] used electrooxidation of kraft lignin in batch and flow cells on Au, Pt, Ni, Cu, and PbO_2 anodes to obtain vanillin. They found that the process was initiated by activated oxygen produced at the electrode. Electooxidation can also be used to treat waste water from pulping processes. The COD of the waste water is reduced by treatment.[12]

The reported yields of low molecular weight products were usually not very high due to the low efficiency of electro-oxidation. In order to solve this problem, some attempts have been made to

improve the type of electrode and the reaction conditions. Platinum, titanium, and nickel have been used for manufacturing the anode. Utley and Smith[9] used nickel as the anode and lead as the cathode in their experiments. Pardini and Smith[13] studied the mechanism of electrooxidative cleavage of lignin at nickel anodes in alkaline electrolytes with model dimers and found that polymerization at nickel anodes was predominant during the degradation procedure although aldehydes were formed together with larger amounts of the corresponding carboxylic acids. They also found that the combinations of 4-hydroxyl, α-keto, β-O-aryl, and β-hydroxymethyl functionality were crucial for the oxidation at nickel.

In anodic oxidation reactions, the material for manufacturing anodes should be cheap and anti-corrosive. It should have a relatively high oxygen-release potential.[14,15] The electrode may be made of the variety of conventionally used materials which are capable of being used in hot alkaline or acidic media. The anode should be of large surface area, and may thus for example be in the form of gauze. PbO_2 membrane electrodes have been shown to meet such demands. The anode had a porous structure by which the electrolyte can penetrate through the electrode by diffusion during the reaction procedure. The porous structure also increases the special surface area of the electrodes, thus improving the efficiency of the reaction.

In this article, electro-degradation of sodium lignosulfonate was performed using a pair of membrane electrodes placed in an electrolytic cell. The average molecular weight of the lignosulfonate was significantly reduced and the surface activity was simultaneously improved. The degradation products, when mixed with petroleum sulfonate, gave low oil–water interfacial tension showing the possibility of being used as a co-surfactant in petroleum recovery. The degradation of 1-(3-methoxy-4-hydroxyphenyl)-2-(2-methoxyphenoxy)ethanol, a β-O-4 lignin model compound, was also conducted to investigate the influences of the reaction variables.

RESULTS AND DISCUSSION

Characterization of the Degradation Products

The electrooxidation of sodium lignosulfonate was conducted at 2.5 V and pH 6 until the electricity consumption reached 20 kC. The product mixture was then fractionated by GPC. The IR spectra of the
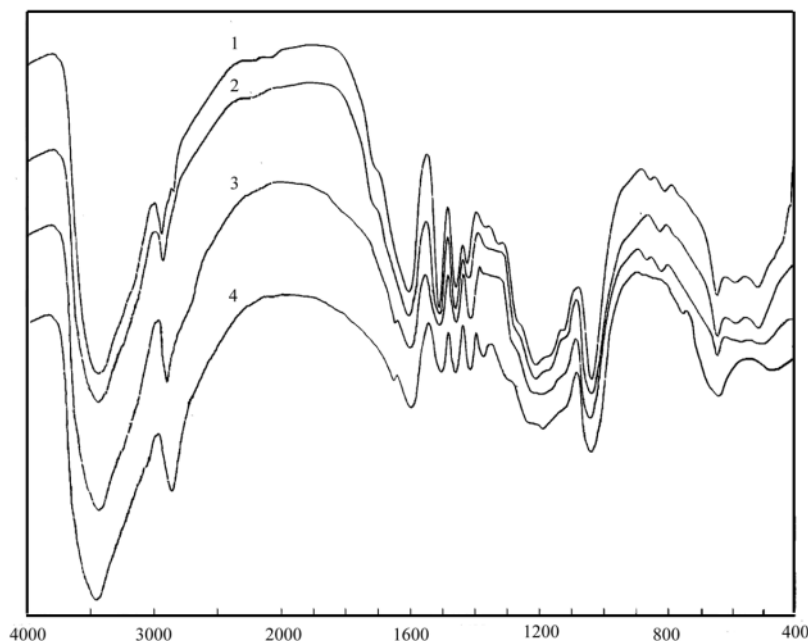
Figure 1. IR spectra of lignosulfonate and its degradation products. (1) Unreacted lignosulfonate; (2) Fraction A; (3) Fraction B; (4) Fraction C.

lignosulfonate and its degradation products are shown in Fig. 1 where Curve 1 represents undegraded sodium lignosulfonate and Curves 2–4 represent three degraded fractions (named as Fractions A, B, and C respectively according to the ascending order of elution volume).

It was found from Curve 2 that the main bands in the infrared spectrum of Fraction A of the degradation product were similar to those of unreacted lignosulfonate. The band at $1675 \, cm^{-1}$ representing the CO groups in conjugation with the aromatic ring, however, became more intensive in IR spectra of the other two fractions, especially Fraction C, indicating that the severely degraded fractions contained more carboxyl groups than the slightly degraded fractions.

The IR spectra of the model compound and its degradation product are shown in Fig. 2. Bands characteristic of aryl ether bonds at 1174 and $1033 \, cm^{-1}$ were weakened after 5 h of reaction indicating the cleavage of the aryl ether bonds.
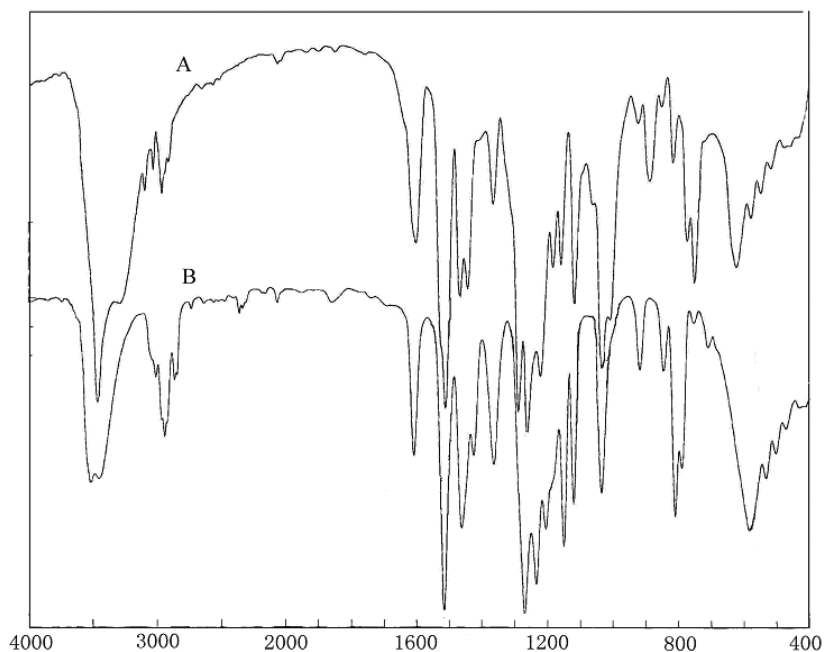
Figure 2. IR spectra of the model compound and its degradation products. (A) model compound, (B) the degradation product.

Reaction Conditions

We found that the voltage, electricity consumption, and pH of the medium had significant effects on the properties of the degradation products.

Voltage

Figure 3 demonstrates that the lignosulfonate displayed a maximum absorption at 280 nm, which is a band characteristic of the aromatic ring of the lignosulfonate. The UV spectra had little variation when the voltage was below 2.0 V indicating that no significant changes had occurred under such conditions. The sulfonate content was kept constant in all the experiments, but the aldehydes and carboxyls varied remarkably only when voltage was above 2.0 V, as shown in Table 1. However, the sulfonic group content did not change significantly. It was also found that the absorption band of the

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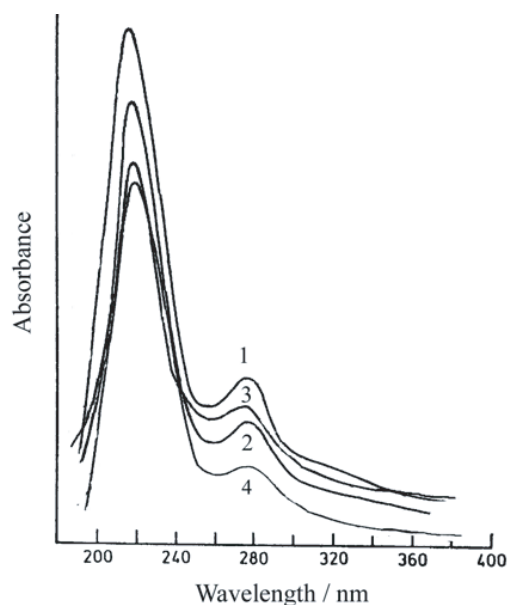
Figure 3. UV spectra of degraded lignosulfonate under different voltages. (1) Undegraded; (2) 1.5 V; (3) 2.0 V; (4) 2.5 V.

Table 1. Influences of voltage on the characteristics of lignosulfonate.

Voltage (V)	0.5	1.0	1.5	2.0	2.5	3.0
Carboxyl (mmol/g)	0.86	0.85	0.87	0.98	0.85	0.79
Sulfonic group (mmol/g)	2.20	2.19	2.19	2.18	2.19	2.18
Phenolic hydroxyl (mmol/g)	1.70	1.71	1.69	1.54	1.40	1.34
Aldehyde (mmol/g)	2.65	2.64	2.66	2.71	2.72	2.55

The electricity consumption was 20 kC.

degradation product at 280 nm decreased when the voltage exceeded 2.5 V. The solution was simultaneously decolored indicating the ring cleavage of lignosulfonate.

Experiments on the model compound gave similar results. IR spectra show that the bands at 1600 and 1510 cm^{-1} were weakened when the voltage achieved 3.5 V. It is estimated that the ring cleavage occurs easily under this condition.

Electricity Consumption

The contents of several functional groups and the average molecular weights of sodium lignosulfonate and its degradation products are summarized in Table 2.

The characteristics of the degradation products were dependent on the electricity consumption. As shown in Table 2 the average molecular weights, together with the contents of some functional groups, also varied with the electricity consumption.

It is interesting that the phenolic hydroxyl, carboxyl, and aldehyde contents increased in the initial stage of the reaction and then decreased after reaching their maximum values (Table 2). The following reasons may be used to explain this phenomenon. The cleavage of aryl ether linkages, which are relatively weak linkages between lignin units, may result in the increase in hydroxyl groups. However, these fragments may then be further oxidized to reduce the total amount of phenolic hydroxyls. Therefore, the content of phenolic hydroxyls was found to increase in the initial stage of the reaction but then decreased in the following stage. Similarly, the alcohols of the lignosulfonate were first converted into aldehydes and subsequently converted into carboxylic acids. For this reason, the content of aldehydic group tended to decrease after achieving a maximum value.

Carboxyl groups formed during the electro-oxidation could also be removed by the cleavage of carbon–carbon bond. Therefore, a decrease in carboxyl content was observed after it reached its maximum value.

The sulfonic group content was fairly constant in the reaction. It seems that sulfonic groups are harder to remove than many other functional groups.

The variations of the content of functional groups of the model compound are shown in Table 3. The data illustrate similar regularities as those with lignosulfonate.

The molecular weight distributions of the lignosulfonate and its degradation products are shown in Fig. 4. As the lignosulfonate had been purified and fractionated before use, the majority of carbohydrates and the low molecular weight fractions of lignosulfonate were removed. Therefore, the GPC chromatogram contains only one peak. However, the GPC chromatogram of each degradation product is comprised of several peaks marked as A, B, C, and D. Fraction A in each product was found to be eluted earlier than the unreacted lignosulfonate, indicating that it represents a condensed fraction. The rest of the components had relatively longer elution times. The peak areas of the low molecular weight fractions increased with time. The data in Table 2 indicate

Table 2. Characteristics of lignosulfonate and its degradation products.[a]

Electricity consumption (kC/g)		0	5	10	15	20
Carboxyl (mmol/g)		0.88	0.95	1.12	0.98	0.85
Sulfonic group (mmol/g)		2.25	2.19	2.23	2.16	2.19
Phenolic hydroxyl (mmol/g)		1.69	1.85	1.72	1.58	1.40
Aldehyde (mmol/g)		2.65	2.76	2.74	2.70	2.72
$\overline{M}_n$	Fraction A	8,930	9,670	11,730	11,670	9,560
	Fraction B		1,800	1,650	1,600	1,330
	Fraction C		650	570	560	550
$\overline{M}_w$	Fraction A	26,630	28,560	29,550	28,570	25,030
	Fraction B		2,100	1,890	1,880	1,800
	Fraction C		720	590	590	570

[a]The voltage of the reaction was 2.5 V.
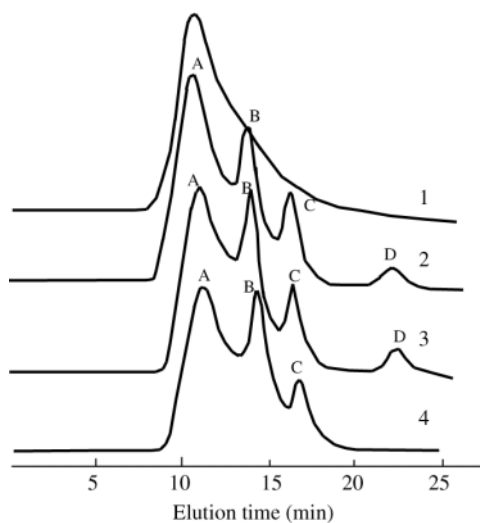
Table 3. Functional group content of the model compound and its degradation products.

	Before reaction	2.3 V, 5 kC/g	2.3 V, 15 kC/g	3.2 V, 5 kC/g	3.2 V, 15 kC/g
Methoxyl (mmol/g)	6.70	6.59	6.48	6.58	6.43
Hydroxyl (mmol/g)	9.82	12.1	13.5	13.1	10.2
Aldehyde (mmol/g)	0.06	0.8	1.3	1.6	1.0

Figure 4. GPC diagram of sodium lignosulfonate and its degradation products. (1) Unreacted lignosulfonate; (2–4) degradation products (2) electricity consumption 10 kC; (3) electricity consumption 15 kC; (4) electricity consumption 20 kC).

that both $\overline{M}_n$ and $\overline{M}_w$ of Fraction A increased at first but then tended to decrease when the electricity consumption achieved 10 kC. It can be concluded that the electro-oxidation contains two stages. A condensation reaction dominates in the first phase and subsequent degradation of the condensation product dominates the second one. Figure 4 also demonstrated that the molecular weight and molecular weight distribution of the degradation products changed with the voltage, the current density and the time. For this reason, we can adjust the molecular weights of the degradation products by changing the voltage, the current density, and the reaction time during the electro-oxidation

process. That is one of the advantages of electro-oxidation over other oxidation methods.

Current Density

The current density should be high enough to break of the linkages between lignin molecules. However, low current density is preferred so that hydrogen and oxygen evolution are minimized and the current efficiency of cleavage by oxidative degradation of the lignin was maximized. According to Utley and Smith[9] over oxidation begins to occur and leads to the formation of gaseous products when the current density is above $10\,mA/cm^2$. We have found that the electrode material was easily broken off from the fibril cloth when the current density exceeded $10\,mA/cm^2$. Relatively low current density, e.g., $6–7\,mA/cm^2$, is preferred in order to minimize excess electrolysis.

In our experiments, each electrode had an area of $48\,cm^2$. Therefore, the current was controlled below $300\,mA$.

pH

It was found that too low a pH of the reaction medium could accelerate the corrosion of the PbO_2 electrode. Too low pH (below 2) could also result in the precipitation of lignosulfonic acid and retard the reaction. The IR spectra in Fig. 5 demonstrate that the bands at 1610 and $1510\,cm^{-1}$ were significantly reduced at pH 10, indicating ring cleavage in the lignin molecules.

Surface Activity of the Degradation Products

During the reaction, some of the relatively weak linkages, e.g., aryl-ether linkages, were cleaved and the average molecular weight was reduced. As shown in Fig. 6, the surface tension of the degradation product was reduced with increasing electricity consumption. As demonstrated in Table 2, the average molecular weight of the ligno-sulfonate decreased with the electricity consumption. It seems that simplified molecular structure and relatively low molecular weight facilitates the improvement in the surface activity. However, no further decrease in surface tension was detected when the electricity consumption
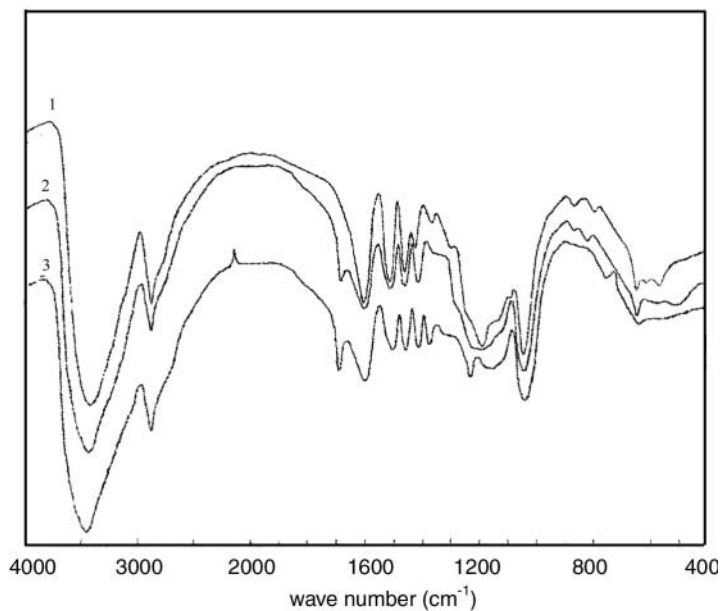
Figure 5. IR spectra of degradation products obtained at different pHs. (1) pH = 4; (2) pH = 7; (3) pH = 10.
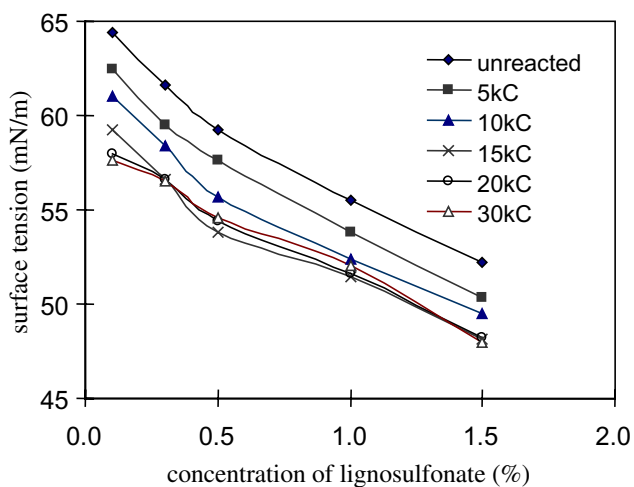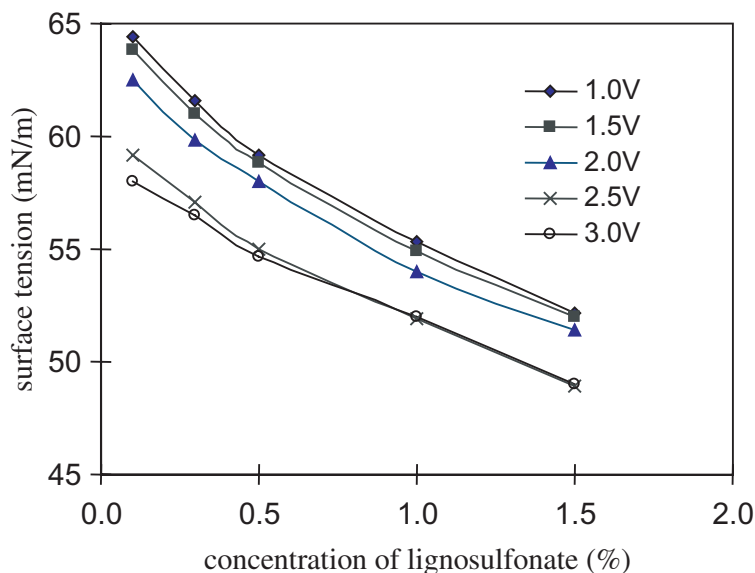

Figure 6. Influence of electricity consumption on surface tension of degraded lignosulfonate (degraded under 2.5 V).

Figure 7. Influence of voltage on surface tension of degraded lignosulfonate. (Electricity consumption: 15 kC.)

reached 30 kC demonstrating that over-electrolysis didn't result in good surface activity.

Figure 7 shows the surface tension vs. voltage relationship of degraded lignosulfonate. No significant change in surface tension was observed when the voltage was below 1.5 V. It seems that slightly degraded ligno-sulfonate didn't possess good surface activity. A sharp reduction in surface tension appeared when the voltage reached 2.5 V indicating degradation under relatively high voltage contributed much to the improvement of surface activity. However, the degradation products formed at 3.0 V didn't have better surface activity than those at 2.5 V.

The variation in absorption at 280 nm in Fig. 3 indicated that the aromatic rings of lignosulfonate were partially cleaved under high volt-age. Such degradation products gave rather poor surface activity. The surface tension of a 1% aqueous solution of the degraded lignosulfonate that was treated at 3.0 V was measured to be 56.5 mN/m. In order to improve the surface activity, the aromatic ring of lignosulfonate should be preserved. A voltage of 2.5 V was sufficient for degradation without leading to excess ring cleavage.
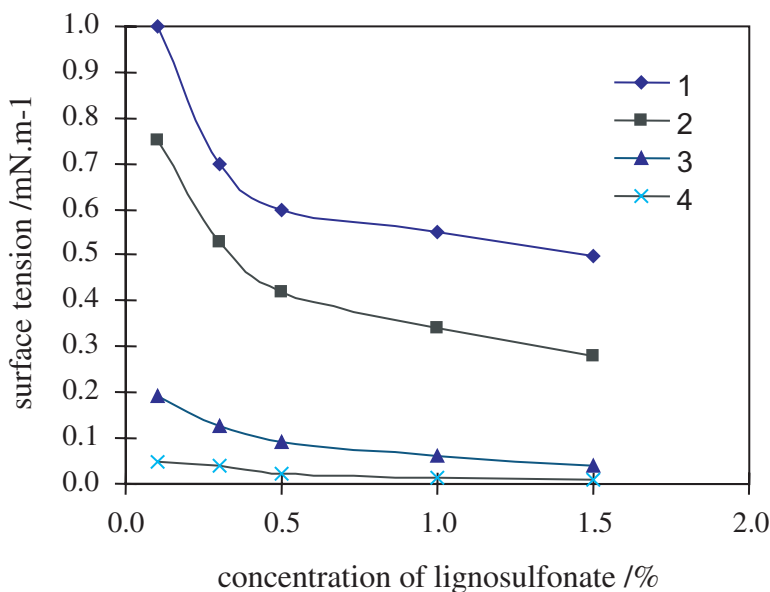
Figure 8. Interfacial tension of lignosulfonate and its degradation products. (1) Sodium lignosulfonate; (2) degradaded sodium lignosulfonate (electricity consumption 15 kC); (3) sample 1 + petroleum sulfonate; (4) sample 2 + petroleum sulfonate.

Figures 6 and 7 also indicate that neither lignosulfonate nor its degradation products achieved ultra-low oil–water interfacial tension. Therefore, they cannot be used as the main surfactants in tertiary oil recovery. However, the surface tension and the interfacial tension were significantly reduced when the lignosulfonate or its degradation products were mixed with 0.3% of petroleum sulfonate (molecular weight 650) to form a binary surfactant system, according to Fig. 8. The interfacial tension between the 0.3% solution of petroleum sulfonate and kerosene was measured to be 0.11 mN/m. The mixed surfactant system, presented much lower interfacial tension than petroleum sulfonate or lignosulfonate. Though not suitable being used as a main surfactant, the degraded lignosulfonate can still be used as a co-surfactant when mixed with petroleum sulfonate. Degraded lignosulfonate gives better performances than the unreacted one, according to Fig. 8.

EXPERIMENTAL

Materials

Sodium lignosulfonate, prepared from the sulfite waste liqor of *Pinus massomiana Lamb*., was a commercial product of Guangzhou Paper Mill, Guangzhou, China. Carbohydrates were removed according to Lin.[16] The carbohydrate content measured to be 4.4%. The purified lignosulfonate was then fractionated by ultrafiltration. The fraction having a number average molecular weight between 1000 and 3000 was used as the starting material.

The model compound, 1-(3-methoxy-4-hydroxyphenyl)-2-(2-methoxy-phenoxy)ethanol, was synthesized by published methods.[20]

The anode was a piece of pretreated polypropylene filter cloth coated with PbO_2. The filter cloth was pretreated with 95% sulfuric acid in order that PbO_2 could accrete on its surface. The cathode was a piece of 200-mesh stainless steel gauze. The sizes of both anode and cathode were $8 \times 6 \, cm^2$. Both electrodes were placed in an electrolytic cell having a dimension of $9 \, cm \times 7 \, cm \times 1 \, cm$, separated by plastic membrane.

Methods

A solution of 5% sodium lignosulfonate solution (30 mL) was added into the electrolytic cell. The pH of the solution was adjusted to 5–8. The reaction was conducted by passing $0.2–5 \, mA \, cm^{-2}$ of current for 5–30 h at room temperature. In each run the voltage of the electro-oxidation was in the range between 0.5 and 3.0 V. The constant current and constant potential electrolyses were performed using a DC power supply and an alvanostat/potentiostat.

The degradation products of sodium lignosulfonate were acidified with dilute hydrochloric acid, extracted with chloroform to remove water-insoluble substances, and then vacuum-dried at room temperature in the presence of P_2O_5.

The electro-oxidation of 1-(3-methoxy-4-hydroxyphenyl)-2-(2-methoxy-phenoxy)ethanol, the model compound, was carried out with a 0.01 mol/L solution of the model compound.

The aldehyde content was determined by the Fehling reaction. The Fehling reagent was added into the diluted electrolyte and the mixture was placed at a boiling water bath. The mixutre was then filtered with cellulose diacetate membrane. The content of aldehyde group was calculated from the mass of Cu_2O formed from the Fehling reagent.

The phenolic hydroxyl content was measured by ion-differential spectroscopy.[17] The difference spectra had ΔD_{max} at 251 and 297 nm.

The sulfonic and carboxylic acid contents were determined by conductometric titration.[18]

Infrared spectra were obtained on an Analect RFX-65A infrared spectrophotometer.

Ultraviolet spectra were obtained on a Specord UV–vis photometer.

The molecular weight and molecular weight distribution was measured on a Waters ALC/GPC 244 apparatus, fitted with a 6000A solvent-delivery system, a Waters Ultrahydrogel 250 column and a Waters 410 differential refractometer. The solvent was 0.05 mol/L LiCl solution having a pH of 6.5. The elution profile was recorded with Baseline 810 interface and data processing software. The molecular weight and the molecular weight distribution were calculated using the log M vs. t_e line of the narrow-distributed Pullulan standard samples.

The surface tension of the lignosulfonate was measured at 25°C according to De Nouy's method.[19]

The interfacial tension between the solution of lignosulfonate (or its degradation product) and kerosene was measured at 60°C on a Krüss Site-04 spinning drop ultralow interfacial tensiometer.

CONCLUSIONS

Sodium lignosulfonate can be converted into several fractions with different molecular weights by electro-oxidation. The amount of lower molecular weight fragments increases with the electricity consumption. The contents of phenolic hydroxyls, carboxyls, and aldehydes increase at first and then tend to decrease.

The minimum voltage necessary for the degradation is found to be 2.0 V. The reaction is accelerated by increasing the voltage. Ring cleavage occurs when the voltage exceeds 3.0 V. The suggested voltage to achieve effective degradation without severe ring cleavage is 2.5–3.0 V. The current density should be below 10 mA/cm^2 to avoid the breaking off of PbO_2 from the membrane.

The surface activity of the lignosulfonate is improved after electro-oxidation. The surface activity can be improved when degraded lignosulfonate is mixed with petroleum sulfonate.

ACKNOWLEDGMENTS

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