Structure—Adsorption Behavior—Dispersion Property Relationship of Alkyl Chain Cross-Linked Lignosulfonate with Different Molecular Weights

Nanlong Hong* and Xueqing Qiu*

ABSTRACT: The structure—adsorption behavior—dispersion property relationship plays a key role in designing a dispersant or surfactant, such as a coal—water dispersant and a water-reducing agent. In this work, was classified into three fractions with narrow molecular weight distributions via the ultrafiltration method. The adsorption behavior of these three fractions was tested via a quartz crystal microbalance with dissipation monitoring, which showed that the adsorption amounts of the three fractions were far higher than that of sulfomethylated lignin. Fraction-1, with the lowest molecular weight, exhibited the greatest adsorption amount on a Au surface under salt-free conditions. This result illustrates that the alkyl chain is more effective for dispersants with low molecular weight to improve its adsorption amount. Fraction-3, with the highest molecular weight, exhibited the greatest adsorption amount on a Au surface under salt-added conditions. This result further illustrates that both the alkyl chain and salt are positive factors for improving the adsorption amount of dispersants. More importantly, the dispersion stabilization of the TiO₂ slurry was significantly improved using the alkAL-S fractions, especially Fraction-3. Based on these results, the alkyl chain cross-linked of lignosulfonate is a promising approach for the industrial applications of lignin as an applicable dispersant.

1. INTRODUCTION

After cellulose, lignin is the second most abundant biopolymer among all the renewable natural resources.¹ In the purest sense, lignin is a three-dimensional, amorphous, and polyphenolic material that originates from three primary precursors: coniferyl, sinapyl, and p-coumaryl alcohols.² Technical lignin, produced from soda pulping processes, is difficult to be utilized efficiently because of its low molecular weight and poor water solubility at a neutral pH.³,⁴ Therefore, technical lignin usually needs to be modified before use in diverse industrial applications.⁵⁻⁸

It is a known fact that the molecular weight (Mₘ) and the sulfonic group content are the key factors that influence the properties of technical lignin and its potential for use as an excellent dispersant in cement,⁹,¹⁰ coal—water slurry,¹¹ pesticide suspension,¹² and so on. To improve Mₘ, methods including formaldehyde condensation polymerization¹³,¹⁴ and graft copolymerization¹⁵⁻¹⁷ are commonly used. To increase the sulfonic group content, methods including sulfonation,⁵,⁶ sulfomethylation,⁷,⁸ and graft sulfonation¹⁸ are used.

The adsorption behavior is the main measurement used by researchers to investigate the dispersion mechanism of lignosulfonate in the suspension system. The conventional research methods used to study the adsorption behavior include UV spectrophotometry¹⁹,²⁰ and electrostatic self-assembly.²¹,²² UV spectrophotometry is a widely applied technology that investigates the amount of dispersants adsorbed on the particle surface, but it cannot detect the conformation of the adsorbed layer. When the electrostatic self-assembly method is used, polycation electrolytes, such as poly(diallyl dimethylammonium chloride), are introduced, and it is difficult to prepare a metastable self-assembled film. Furthermore, both these methods suffer from the inability to measure the adsorption behavior in real time. Thus, finding a better way to investigate these dispersion mechanisms in real time is critical. Quartz crystal microbalance with dissipation monitoring (QCM-D) is a fundamental and efficient research method for better detecting the adsorption amount in real time and conformation of the adsorbed layer.²³⁻²⁵ Therefore, QCM-D was applied to test the adsorption behavior in our paper.

The results of previous studies showed that the adsorption amount of a high-Mₘ lignin polymer is greater than that of a low-
investigated. Moreover, the dispersion stabilization of TiO₂ was readily improved by introducing an alkyl chain into lignosulfonate (LS) to improve the Mₚ of lignin via the alkyl chain cross-linked polymerization method. This method is more efficient and convenient to improve than the other reported methods for improving the Mₚ of lignin.²⁻¹⁷ Ultrafiltration (UF) of lignosulfonate is an efficient method to obtain lignin-based polymers with narrow Mₚ distributions.²⁷⁻³⁵ Therefore, a UF device was applied to purify and classify alkyl chain cross-linked lignosulfonate (alkLS) to obtain different fractions with narrow Mₚ distributions, denoted as Fraction-1, Fraction-2, and Fraction-3, and the adsorption behaviors of the three alkLS fractions on the Au surface were measured by QCM-D. Unexpectedly, the effect of the alkyl chain on the adsorption behaviors of the three fractions is distinct. The effect of ionic strength on the adsorption behavior was further investigated. Moreover, the dispersion stabilization of TiO₂ was significantly improved using the three fractions. Therefore, in our study, the adsorption amount and dissipation factor could be readily improved by introducing an alkyl chain into lignosulfonate, and excellent and suitable dispersants could be designed for industrial applications.

2. RESULTS AND DISCUSSION

2.1. Molecular Weight Distributions of the alkLS Fractions. The Mₚ distributions of the initial AL-S and alkLS are presented in Figure 1a. The average Mₚ and the polydispersity index (PDI) are also given in Table 1. The molecular weight of alkLS is remarkably increased via alkyl chain-bridged polymerization. The Mₚ of alkLS (61,200 Da) is approximately 11.3 times higher than that of AL-S (5400 Da). The results of the functional group content show that the phenolic content of alkLS decreased remarkably (from 2.21 to 0.51 mmol/g).

The effect of the UF method on the Mₚ distribution of alkLS is shown in Figure 1b. The value PDI of alkLS is wide, although the Mₚ increased noticeably (see Figure 1a). Based on the UF method, the Mₚ distribution of the fractions separated by three membranes is very narrow and symmetric (see Figure 1b). The results of the Mₚ distribution are also provided in Table 1. All the three fractions have a low PDI in the range of 1.49–1.81. The average Mₚ’s of Fraction-1, Fraction-2, and Fraction-3 are 5800, 43,600, and 152,000 Da, respectively. The results are relatively equivalent to the membrane characteristics applied to classify alkLS.

The functional group contents of the alkLS fractions were assessed, as shown in Table 1. Increasing the Mₚ, the functional group contents of the three fractions decreased, including –OH, –SO₃H, and especially –OH. The elemental analyses of the three alkLS fractions were also investigated in our study (see Table 2). As expected, the content of C and H increased, and the S content decreased with the increasing Mₚ of fractions. The results are consistent with the results of the functional group contents.

2.2. Structural Characterization. To better elucidate the structural characteristics of the three alkLS fractions, spectroscopic analyses, including Fourier transform infrared (FTIR) and ¹H nuclear magnetic resonance (NMR), were performed (see Figure 2). The interpretations of the FTIR spectra are shown in Figure 2a. The broad band at approximately 3450 cm⁻¹ corresponds to O–H elongation, and the peaks at 2937 and 2860 cm⁻¹ are due to the methylene stretching vibrations of the alkyl chain of C₆H₄·Br₂. As the Mₚ of the alkLS fractions increased, the intensity of A₁₃₅₀ decreased, whereas that of A₂₉₃₇ increased gradually; this result is in agreement with the functional group content results.
The $^1$H NMR spectra of the three fractions are presented in Figure 2b. The signals between 0.5 and 2.0 ppm are ascribed to aliphatic chain protons. The signal intensity of the aliphatic H exhibits a strong positive correlation with the increasing $M_w$ of the alkAL-S fractions. The results are also consistent with the IR results. Therefore, through the series of characterizations of the alkAL-S fractions separated from the three membranes, the UF method is a feasible and powerful technique to obtain alkAL-S fractions with a very low polydispersity.

### 2.3. Film-Forming Properties and Wetting Properties on Au Surface.

To investigate the effect of the alkAL-S fractions with different $M_w$'s on the particle distribution of aggregates, the film-forming morphology of the three fractions on a Au surface was observed by atomic force microscopy (AFM). As can be observed in Figure 3a–c, Fraction-1, with the lowest $M_w$, has the minimum surface roughness (root mean square, RMS), and RMS increases gradually as the $M_w$ of the three fractions increases. Moreover, the morphology shows that the particle size gradually increases from Fraction-1 to Fraction-3. These results illustrate that the aggregation level becomes higher with the increasing $M_w$ of the alkAL-S fractions.

The wetting properties of the three alkAL-S fractions on a Au surface were all assessed by contact angle measurements. As can be observed in Figure 3d–f, the contact angles of the alkAL-S fractions on Au gradually increase from Fraction-1 to Fraction-3. This result indicates that the affinity of Fraction-1 for the Au surface is relatively higher than that of Fraction-2 and Fraction-3 for the Au surface.

### 2.4. Adsorption Behavior Measurement by QCM-D.

The adsorption behavior of the three alkAL-S fractions on a Au surface was investigated by QCM-D. QCM-D is an efficient tool that provides information about the adsorption amount, adsorbed layer conformation, and viscoelasticity changes. The adsorption amount of the alkAL-S fractions could be detected by determining the decrease in frequency ($\Delta F$); the conformation and viscoelasticity of the adsorbed layer could also be observed by evaluating the changes in dissipation ($\Delta D$). As shown in Figure 4a, we investigated the adsorption behavior of the samples at a concentration of 1 g/L under salt-free conditions; the adsorption amount of AL-S was the lowest because of its strong hydrophilicity. The results showed that the adsorption amounts of the three alkAL-S fractions increased compared with that of the straw material AL-S. As proposed in Figure 6, an alkyl chain was introduced to the AL-S molecules to improve the compatibility of the alkAL-S fractions. More importantly, Fraction-1 exhibited the highest adsorption amount and dissipation factor, which were even greater than that of lignosulfonate. The adsorption amount decreased with the increasing $M_w$ of the alkAL-S fractions. This result occurred mainly because of the structural difference among the three
alkAL-S fractions (see Figure 6). As seen from Figure 6, the size of the aggregates in Fraction-1 is smaller than that of the other two fractions, and therefore, the alkyl chain more effectively shields the electrostatic repulsions between the sulfonic groups in Fraction-1 than in the other fractions. The desorption of the samples is also investigated in Figure 4a, in which AL-S exhibits larger desorption amounts than the three alkAL-S fractions.

The adsorption process of the three alkAL-S fractions was estimated by plotting the change in $\Delta D$ as a function of the changes in $\Delta F$, and the plot was called the $D-F$ curve (see Figure 4b). The slope of the $D-F$ curve could be used to illustrate the conformation and viscoelasticity of the adsorbed layer and the affinity of the sample to a Au surface. As illustrated in Figure 4b, the slope of the AL-S curve is larger than that of the three alkAL-S fraction curves, and furthermore, the slopes of the alkAL-S fraction curves increased from Fraction-1 to Fraction-3. These results suggested that there was a more compact conformation and a stronger affinity between Fraction-1 and the Au surface. The conformation of the adsorbed layer of Fraction-3 is obviously looser than that of the other two fractions.

As investigated in Figure 3, the aggregation levels of the alkAL-S fractions become higher with the increasing $M_w$ of the alkAL-S fractions, and the affinity of Fraction-1 for Au is relatively stronger than that of Fraction-2 and Fraction-3, which makes Fraction-1 preferred for adsorption on a Au surface to form a compact adsorbed conformation. The adsorption morphology of the three alkAL-S fractions adsorbed on a Au surface was also observed by AFM, as shown in Figure 5. We found that the conformation and size of the nanoaggregates were different for each of the fractions. A very compact adsorbed layer consisting of nanoaggregates was observed for Fraction-1 (see Figure 5a). The aggregate sizes of Fraction-2 and Fraction-3

Figure 4. Adsorption analysis results of the three alkAL-S fractions on a Au surface under a salt-free condition by the QCM-D method. (a) Change in frequency and dissipation (the rinsing step is also shown in the curves). (b) Changes in dissipation as a function of the change in frequency.

Figure 5. Adsorption morphologies of the three alkAL-S fractions on a Au surface: (a) Fraction-1, (b) Fraction-2, and (c) Fraction-3 (top image dimensions: $3 \times 3 \ \mu m$; bottom image dimensions: $1 \times 1 \ \mu m$).

Figure 6. Proposed adsorption mechanism of AL-S and the three alkAL-S fractions adsorbed on a Au surface under the salt-free condition.
were relatively larger than that of Fraction-1, and the nanoaggregates of Fraction-1 were more compact than those of the other two fractions, both of which contributed to the remarkable adsorption amount and low viscoelasticity of Fraction-1 on a Au surface.

2.5. Effect of Ionic Strength on the Adsorption Behavior. In our study, we also investigated the effect of ionic strength on the adsorption behavior of the alkAL-S fractions on the Au surface. A 0.5 M NaCl salt concentration was applied in the sample solutions. As seen from Figure 7a, the adsorption amounts of all the three alkAL-S fractions increased compared with those of the salt-free solution and were even greater than those that were previously reported.24 This result occurred mainly because the salt shielded the electrostatic repulsions between the sulfonic groups.22 We also noted that the adsorption amount of Fraction-3 was the greatest, but the adsorption amount of Fraction-2 was lower than that of Fraction-1. The results may be explained as follows. First, the $M_w$ distributions of the alkAL-S fractions are remarkably narrow and symmetric, which is conducive to preparing the uniform nanoaggregates. Second, although the particle size of Fraction-2 is larger than that of Fraction-1, the nanoaggregates formed in Fraction-1 were more compact than those in Fraction-2. Therefore, based on the above mentioned factors, the adsorption amount of Fraction-1 is greater than that of Fraction-2 but lower than that of Fraction-3. The desorption process of all the alkAL-S fractions was also investigated after the adsorption equilibrium was achieved (see Figure 7a). We found that all the alkAL-S fractions exhibited larger desorption amounts after rinsing compared with the salt-free solution. This result occurs because the density and viscosity of the solution increased after the NaCl salt was added, which makes the adsorbed layer on the Au surface more viscoelastic than that achieved under salt-free conditions.

The dissipation as a function of changes in the frequency in the adsorption processes of the three alkAL-S fractions was also estimated, as shown in Figure 7b. Unexpectedly, the slopes of the three fraction curves are very close. This result indicated that the conformation of the adsorbed layers from Fraction-2 and Fraction-3 had become more compact. We also compared the slopes of the curves obtained with the salt-free and salt-added conditions. All the slopes increased after 0.5 M NaCl was added, indicating that the conformations of the adsorbed layer became looser, and the viscoelasticity of the layer increased.

The adsorption morphology of the three alkAL-S fractions after 0.5 M NaCl was added on the Au surface was also observed by AFM, as shown in Figure 8. The aggregation levels of the three fractions improved, and the height of the adsorbed layer noticeably increased. These results further indicated that NaCl could shield the electrostatic repulsions and promote the aggregation of the alkAL-S fractions.

2.6. Dispersion Properties in TiO$_2$ Slurry. The adsorption property plays an important role in the dispersion properties of dispersants in suspension systems, such as TiO$_2$. TiO$_2$ is widely applied as a mineral oxide in pigments and paints and as nanomaterials.38,39 Because of their large surface areas, TiO$_2$ particles easily form agglomerates, which negatively affects their performance in industrial applications. Therefore, dispersants are applied to improve the dispersion stabilization of TiO$_2$ particles, which is very important for their industrial applications.

As seen in Figure 9, the dispersion property of the TiO$_2$ slurry was relatively improved using AL-S compared with that obtained with no additives (blank). When the three alkAL-S fractions were applied to the TiO$_2$ suspension slurry, the dispersion stability of the TiO$_2$ slurries containing the alkAL-S fractions improved significantly and was better than that of the TiO$_2$ slurry containing AL-S. We found that the $M_w$ of Fraction-1 was close to that of AL-S, but the adsorption and dispersion properties of Fraction-1 were both better than those of AL-S. This result occurred because the alkyl chain in Fraction-1 improved the affinity for the Au surface and provided steric hinderance between the TiO$_2$ particles. On the other hand, Fraction-3 exhibited the best dispersion property in TiO$_2$ compared with the other fractions because of its moderate sulfonic group content and high $M_w$, which improved the steric hinderance and electrostatic repulsion between the sample-coated TiO$_2$ particles.

3. CONCLUSIONS

To summarize, alkyl chain cross-linked lignosulfonate (alkAL-S) was prepared from a pulping liquor and applied to classify and obtain three different fractions with a narrow $M_w$ distribution via a UF method. Gel permeation chromatography (GPC), FTIR, and $^1$H NMR measurements were performed to investigate the molecular structure of these three fractions. We found that alkAL-S with different fractions exists as nanoaggregates with different particle sizes. The adsorption properties determined via QCM-D showed that the adsorption amounts of the three fractions were far higher than that of AL-S. Fraction-1 exhibited the greatest adsorption amount on a Au surface under a salt-free condition. This result illustrates that the alkyl chain is more
effective for a dispersant with a low $M_w$ to improve the adsorption amount. Fraction-3 exhibited the greatest adsorption amount on a Au surface under a salt-added condition. This result further illustrates that both the alkyl chain and salt are positive factors to improve the adsorption amount of dispersants. More importantly, the dispersion stabilization properties of the TiO$_2$ slurry were improved significantly using the three alkAL-S fractions, especially Fraction-3. Based on these results, the alkyl chain cross-linking of lignosulfonate is a promising approach for using lignin as an applicable dispersant in industrial applications.

4. MATERIALS AND METHODS

4.1. Materials. Wheat straw alkali lignin (WAL) was supplied by Shuntai Paper Pulping Co., Ltd. (Shuntai, Hunan, China). 1,6-Dibromohexane ($C_6H_{12}Br_2$) with a purity of 97% was supplied by Energy Chemical (Shanghai, China). All other chemicals were of analytical grade, including formaldehyde ($CH_2O$) of 37%, sodium hydroxide (NaOH), sodium sulfate (Na$_2$SO$_3$), potassium iodide (KI), and hexane. Titanium dioxide (TiO$_2$) powder was a commercial product obtained from Kermel Chemistry Co., Ltd. (Tianjin, China).

4.2. Preparation of Alkyl Chain Cross-Linked Lignosulfonate (alkAL-S). WAL was dissolved in an alkaline NaOH solution with a pH of approximately 10. Formaldehyde was added slowly to the reaction solution at 70 °C for 20 min. Then, the temperature was heated to 95 °C, and sodium sulfate was added subsequently. Then, the reaction was maintained at 95 °C for 3 h. When the temperature was cooled to 80 °C, a $C_6H_2Br_2$ reagent and a trace amount of KI were added to the reaction solution, and NaOH was used to maintain a pH of 12. The polymerization reaction was stopped after the solution was refluxed at 80 °C for 9 h. The sample was then extracted with hexane to remove the excess $C_6H_2Br_2$, and the polymer in the aqueous solution was obtained.

4.3. UF of alkAL-S To Obtain Different Fractions. The UF fractions were obtained using an UF201 ultrafiltration apparatus (Wuxi Membrane Science and Technology Corp., China). UF membranes with molecular weight cutoffs of 10, 50, and 100 kDa were used in our study. Finally, alkAL-S was classified into three fractions: Fraction-1 (10−50 kDa), Fraction-2 (20−100 kDa), and Fraction-3 (>100 kDa).

4.4. Structural Property Characterization. 4.4.1. $M_w$ Measurements. The $M_w$ distributions of the UF fractions were determined by aqueous GPC. The calibration standard was polystyrene sulfonate with a $M_w$ ranging from 2 to 150 kDa. The eluent was a 0.10 M NaNO$_3$ solution introduced with a flow rate of 0.50 mL/min. All the samples were dissolved and diluted to achieve a 0.3 wt % concentration using double-distilled water and filtered with a 0.22 μm filter. The UV absorption at 280 nm was monitored with a Waters 2487 UV detector (Waters Co., Milford, MA).

4.4.2. Functional Group Content and Elemental Analysis. The phenolic hydroxyl group (−OH) content of the UF fractions was determined by the Folin–Ciocalteu colorimetric method. The sulfonic group (−SO$_3$H) content of all the samples was determined by an automatic potentiometric titrator (Type 809 Titrand, Metrohm Corp., Switzerland).

Figure 8. Adsorption morphologies of the three alkAL-S fractions on a Au surface with a 0.5 M NaCl solution: (a) Fraction-1, (b) Fraction-2, and (c) Fraction-3 (top image dimensions: 3 × 3 μm; bottom image dimensions: 1 × 1 μm).

Figure 9. Dispersion properties of AL-S and the three alkAL-S fractions on the TiO$_2$ slurry.
analyses of all the fraction samples were performed by an Elementar vario EL cube.

4.4.3. Infrared Spectroscopy Analysis. The FTIR spectra of the UF fractions were measured with an Autosystem XL/I-series/Spectrum2000 instrument (Thermo Nicolet Co., Madison, WI). The measurement method using the potassium bromide pressed-disc technique was followed.

4.4.4. 1H NMR Spectroscopy Analysis. The 1H NMR spectra of the three fractions were recorded with 30 mg of each sample dissolved in 0.5 mL of dimethyl sulfoxide-d$_6$ at room temperature by a DRX-400 spectrometer (Bruker Co., Ettingen, Germany).

4.4.5. Film-Forming Properties of the Different Fractions. The three alkAL-S fractions were spun on an Au surface with a mass concentration of 1 g/L. The film-forming properties were studied by AFM.

4.4.6. Contact Angle Measurements. The wetting properties of the alkAL-S fractions separated from the three different membranes were measured by drop shape analysis (JC2000C1) using a mass concentration of 1 g/L on the Au surface.

4.5. Adsorption Behavior Measurement by QCM-D. The adsorption properties of the alkAL-S fractions on the Au surface were evaluated by QCM-D (instrument Q-Sense, Vastra Frolunda, Sweden). The sample solutions, with a mass concentration of 1 g/L under the salt-free and 0.5 M NaCl conditions, were added with a continuous flow rate of 150 µL/min into the QCM-D chamber at 25 °C.

4.6. Dispersion Properties. The dispersion stabilization properties of AL-S and the three alkAL-S fractions in TiO$_2$ slurries were investigated using Turbiscan Lab Expert (Formulation, L’Union, France). A 3 wt % TiO$_2$ powder was slowly mixed with the 0.5 wt % samples in deionized water. Then, the TiO$_2$ slurry was stirred at 100 rpm for 10 min and measured by Turbiscan. The scan rate was one scan every 2 min, and the total scan time was 2 h.

**AUTHOR INFORMATION**

Corresponding Authors

Nanlong Hong — School of Chemical Engineering and Energy Technology, Dongguan University of Technology, Dongguan 523808, China; orcid.org/0000-0002-6019-7234; Email: hongnl@dgut.edu.cn

Xueqin Qiu — School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China; Email: xueqinqiu66@163.com

Complete contact information is available at https://pubs.acs.org/10.1021/acsomega.9b03535

Notes

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