INFLUENCE OF LIGNOSULFONATES ON THE PROPERTIES OF DIMETHOMORPH WATER-DISPERSIBLE GRANULES

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Different molecular weight fractions of lignosulfonates (LS), LS having different cations, and modified LS with different degree of sulfonation and intrinsic viscosity were prepared and used as dispersants for Dimethomorph water-dispersible granules (DWG). The suspending ratio of DWG was tested to evaluate the effectiveness of LS as a dispersant. Moreover, the stability of DWG suspensions was measured by a new instrument (Turbiscan LabExpert). The suspending ratios of DWG having different molecular weight fraction of LS increased with increasing molecular weight in a suitable range. The kind of cation associated with the LS didn't have an obvious influence the effectiveness of LS as a dispersant. Furthermore, the higher degree of sulfonation of LS, of which the intrinsic viscosity was similar, the better was its effectiveness as a dispersant. When the intrinsic viscosity increased within a suitable range, the effectiveness of LS as a dispersant increased. Similar findings were achieved by evaluating the stability of DWG suspensions with all the LS as dispersants, and larger molecular weight could decrease the growth of particle size.

Keywords: Lignosulfonates; Water-dispersible granules; Degree of sulfonation; Molecular weight; Cation

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INTRODUCTION

Water-dispersible granules (WG), a new type pesticide formulation, has been developed as a safer and more attractive alternative to wettable powders (Ding 2004; Knowles 2001). The market occupancy of this formulation is increasing due to its convenience of packaging and usage, which requires no solvents, is dustless, has low inhalation hazard to the applicator, and provides freely flowing granules (Ling 2003). A suspension can be formed by some agitation when WG is added into water, and the suspension will maintain a uniform spray mixture. The formulation contains a high percentage (often 75% to 90%) of active ingredients of pesticide and adjuvants, which are added principally to increase the active ingredients efficacy and reduce phytotoxicity. The adjuvants include wetting agents, dispersants, spreaders, carriers, and so on. The addition of dispersants can make the active ingredient mix with water more effectively, increase the stability of suspension, and also make the active ingredients spread evenly over the plant surface. The dispersants preferably used in present WG formulations include alkyl naphthalene sulfonates, lignosulfonates, and polycarboxylates, etc. (Ding 2004).

Lignosulfonates (LS) are a by-product of sulphite cellulose pulp production; they contain hydrophilic groups which makes them water-soluble (Dawy et al. 1998; Telysheva et al. 2001; Wang 2002). They can be described as anionic surfactants. They are relatively low in cost and widely used in many application areas (Li et al. 2007; Matsushita et al. 2005; Pei et al. 2008). They are applied as water reducers in concrete, as dispersants in coal-water slurry, and in textile dyeing and agrochemicals (Chen and Lin 2005; Lundstedt and Alan 1999; Minoo and Nishinomiya 2003; Moorer et al. 1976). LS is the dominant dispersant used for pesticide formulations in worldwide markets (Ding 2004). Some researchers have reported (Matsushita et al. 2005; Ouyang et al. 2006; Qiu et al. 2005) that the degree of sulfonation and molecular weight of LS are important factors influencing its performance. However, relatively little has been published regarding the relationships between structure properties of LS and its performance as a dispersant for WG.

In this paper, LS with different molecular weights were prepared by ultrafiltration separation (Ouyang et al. 2006), and LS with different cation content were obtained by ion-exchange reaction. Furthermore, a series of modified LS with different degree of sulfonation or molecular weight were acquired by sulfonation and copolymerization. All of the products were used as dispersants to prepare Dimethomorph Water-dispersible Granules (DWG). The main purpose of this research was to improve properties of LS by molecular weight control and structure modification. This would provide an effective direction to modify LS into a high performance dispersant.

A new dispersion stability analytical instrument, the Turbiscan LabExpert, has been developed by Formulaction Corp., a French company, to analyze the physical destabilization of concentrated dispersions (suspensions, emulsions, foams, etc.) (Chanamai and McClements 2000; Mengual et al. 1999). It has the advantages of being nondestructive, as well as detecting directly and more effectively. In this paper, the device was adopted to analyze the destabilization of dilute suspensions of WG. It is well known that beams of light shining in a suspension would be scattered by the particles. According to Mie Theory (Borhen 1983), the light intensity is dependent on the particle size and volume fraction of a suspension. Thus the particle migration and particle size variation (Chanamai and McClements 2000; Mengual et al. 1999) could be calculated.

EXPERIMENTAL

Materials

Dimethomorph (Cohen et al. 1995) is a systemic morpholine fungicide for downy mildews, late blights, crown, and root rots for grapes, potatoes, tomatoes, and other vegetables, and in this paper it was obtained from JIANGSU Frey Agrochemicals Co. Ltd., China with a minimum purity of 95.0%. The other adjuvants included sodium dodecyl sulfonates (SDS) and ethyl-naphthalene sulfonates. The commercial LS, sodium lignosulfonates (SLS) and calcium lignosulfonates (CLS), were purchased from ShiXian Paper Making Co. Ltd., China.

Ultrafiltration of Lignosulfonates

CLS was fractionated by ultrafiltration, using a hollow fibre membrane ultrafiltration apparatus (Hangzhou Water Treatment Factory, China) (Ouyang et al. 2006). The cut-off molecular weights of the membranes were 1,000, 5000, 10,000, and 30,000. Correspondingly, the molecular weights of the fractions were less than 1,000 (fraction 1), 1,000-5,000 (fraction 2), 5,000-10,000 (fraction 3), 10,000-30,000 (fraction 4), and larger than 30,000 (fraction 5). All the five fractions were used as dispersants for preparing DWG.

Ion-Exchange of Lignosulfonates

LS having different cations were acquired by ion-exchange from CLS with sodium carbonates, magnesium sulfates, and ferric sulfates respectively. The products were named by Na-LS, Mg-LS, and Fe-LS. The products were used as dispersants for producing DWG.

Modification of Lignosulfonates with Different Degree of Sulfonation and Molecular Weight

A certain amount of SLS was solubilized by water in a flask bottle equipped with an electric heating device, a motor stirrer, a thermometer, a dropping funnel, and a reflux condenser. Hydrogen peroxide was added to pre-oxidize SLS under the pH of 10 to 11, and then Na_2SO_3 was added to cause sulfonation at $85^{\circ}C$, and finally formaldehyde was added dropwise to copolymerize with the sulfonated SLS. The reaction products were cooled to ambient temperature and then dried to powder.

The polymer intrinsic viscosity ($[\eta]$) was positively correlated with molecular weight according to the Mark-Houwink equation (Chuah et al. 2001): $[\eta] = kM^{\alpha}$ (where k and α are constants specific to the solvent and temperature, and M is molecular weight). In this work, the intrinsic viscosity of modified product was used to characterize its molecular weight. The modified SLS with different $[\eta]$ and degree of sulfonation were acquired by adjusting the amounts of formaldehyde and Na_2SO_3. These products were used as dispersants for preparing DWG.

Stability Measurement of DWG Suspension

A Turbiscan LabExpert device was used to measure the stability of DWG suspensions with different LS as dispersants. The measurement principle is as follows (Chanamai and McClements 2000; Mengual et al. 1999): As a beam of light shines in a suspension, it will be scattered by the particles in the suspension. There is a detector receiving the light scattered backward from the particles. The backscattered light intensity depends on the particle volume fraction and particle size. It increases with rising particle volume fraction when the particle size is constant and the volume fraction is larger than critical volume fraction (Φ_c=0.08%). On the other hand, it decreases with increasing particle size when the volume fraction is constant and the particle size is larger than the critical particle size (d_c=0.3μm). According to the backscattered light intensity, we can estimate the destabilization of the suspension.

The measurement procedures were conducted as follows: A certain amount of DWG was disintegrated in water to form a suspension in which the particle volume

fraction (Φ=1.5%) was larger than Φ_c and the particle size (d>3μm) was much larger than d_c. The suspension was placed into a flat-bottomed cylindrical glass tube (60 mm height, 15 mm internal diameter). The backscattered light from suspensions was measured as a function of height at different times. When the measurements were completed, the signals were treated by the software (TLAB EXPERT), which handled the data and computer dialogue. The results were presented as the full profiles (backscattered light intensity versus heights at different time).
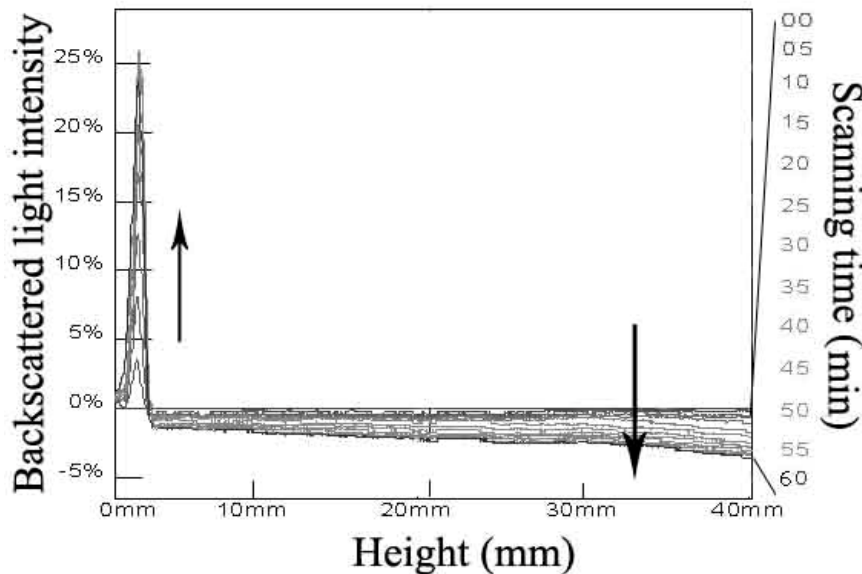

Fig. 1. Backscattered light intensity versus heights of DWG suspension at different time

Figure 1 shows the backscattered light intensity of the DWG suspension with fraction 4 as dispersant versus heights at different time (the arrow points the direction of curves with time increasing). As shown in Fig.1, the backscattered light intensity decreased with time at the top (~40mm) of the suspension, but increased with time at the bottom (~0mm) of the suspension. It was obvious that the particles volume fraction decreased at top but increased at bottom, indicating that particles had migrated from top to bottom. After calculations were performed by the software TLAB EXPERT, the sediment thickness of the suspension during the measuring period of 60 minutes could be acquired (Chanamai and McClements 2000). As shown in Fig. 2, the sediment thickness of the suspension increased with increasing time and finally it was 0.38mm.

As also can be seen from Fig. 1, the backscattered light intensity decreased with time at the middle (~20mm) of the suspension. At a certain time a thin layer was chosen, in which the original particles moved downwards and the new particles moved into this layer from the upper suspension. So the volume fraction could be taken as a constant. According to the measurement principle, the particles size must be enlarged (Borhen 1983). After computations by the software TLAB EXPERT, the particle size variation during the measuring period of 60 minutes could be acquired (Chanamai and McClements 2000). As shown in Fig. 2, the particle size of the suspension increased with the passage of time. The initial particle size of the suspension was 3.86μm, and the final particle size of the suspension was 4.67μm; thus, the particle size growth during the measuring period was 1.03μm.
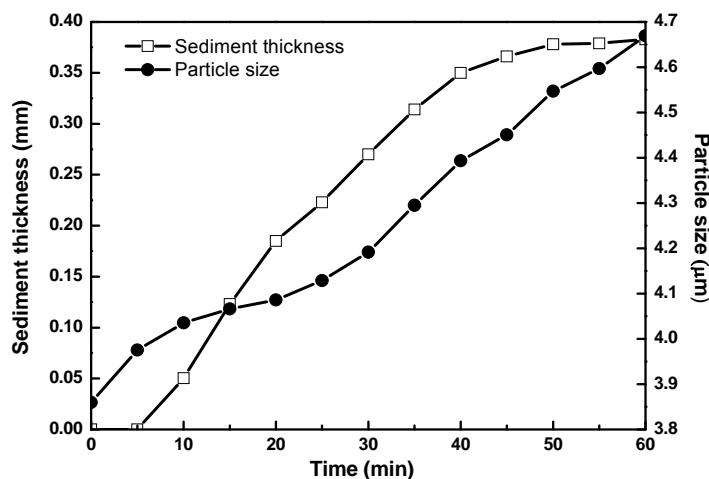
Fig. 2. Sediment thickness and particle size variation of DWG suspension with passage of time

RESULTS AND DISCUSSION

Suspending Ratio of DWG with Different Fractions of CLS

When WG is dispersed in water, the insoluble active ingredient will move downwards by gravity. The suspending ratio is defined as the ratio of suspended mass of active ingredient at a certain time to its original total mass, which indicates the dispersion status of the suspension (Ding 2004). In this paper, the active ingredients was Dimethomorph, and its content was measured by HPLC (Yang Jianxiang et al. 2003). Joseph and Jumes (1982) investigated LomarD with different molecular weight as dispersants for WG and found the suspending ratio increased with molecular weight when it was more than 700. In the present work the effects of molecular weight of LS on the suspending ratio of DWG were investigated. The five fractions separated by ultrafiltration from CLS were used as dispersants for DWG, and the suspending ratios of DWG were tested.
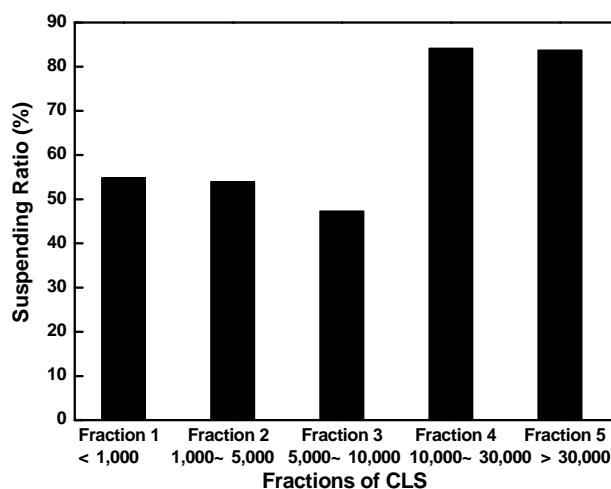

Fig. 3. Suspending ratio of DWG using different fraction of CLS as dispersants

It can be seen from Fig. 3 that the suspending ratio of DWG using fractions 1 to 3 was low (~50%) and decreased with increasing molecular weight of CLS. But it increased to 84.18% and 83.77% when the dispersant was fraction 4 and fraction 5 respectively. When pesticide particles adsorb ionic dispersants onto their surface, the electrostatic effects and steric stabilization effects (Ren et al. 2005) could be formed to prevent the particles from aggregating with each other. As the molecular weight of CLS increased, the Van der Waals force between the molecules of CLS and Dimethomorph would be larger. So it was easier for the higher mass material to be adsorbed on Dimethomorph surfaces, and its longer chains help to enhance the steric effects and prevent particles aggregation more efficiently. Thus the suspending ratios of DWG with fraction 4 and fraction 5 were higher than the others. These findings indicated that the effectiveness of CLS as a dispersant increased with rising molecular weight of CLS. However, the electrostatic effects were influenced mostly by the degree of sulfonation of CLS, which changed with different fraction of CLS, and this might be the reason that the suspending ratio of DWG decreased at first.

Stability of DWG Suspension with Different Fraction of CLS

The small particles in a suspension have high surface energy, which will cause the particles to aggregate spontaneously (Mengual et al. 1999). In addition, if they are large enough and denser than the suspending medium, the particles would migrate downwards under the effect of gravity. These two behaviors will break the stability of suspension and further influence the efficacy of active ingredients (Ren et al. 2005). The stability of DWG suspension prepared with different fraction of CLS was measured by Turbiscan LabExpert. The total profiles of these suspensions were similar with Fig.1. After being handled as described in the Experimental section, the sediment thickness and particle size variation of these suspensions were obtained, and the results are listed in Table 1.

Table 1. Stability of DWG Suspension with Different Fractions of CLS

Suspension with different fractions	Sediment thickness /mm	Initial particle size /μm	Final particle size /μm	Particle size growth /μm
Fraction 1 (< 1,000)	0.42	5.79	7.77	1.98
Fraction 2 (1,000 ~ 5,000)	0.42	5.65	7.25	1.60
Fraction 3 (5,000 ~ 10,000)	0.41	4.33	5.72	1.39
Fraction 4 (10,000 ~ 30,000)	0.38	3.86	4.67	1.03
Fraction 5 (> 30,000)	0.40	4.75	5.79	0.81

As can be seen from Table 1, during the measuring period the sediment thickness and particle size of these suspensions decreased with increasing molecular weight of CSL. When the molecular weight of CSL increased to 10,000~30,000 (fraction 4), the sediment thickness of this suspension was 0.38mm, which was the lowest, and the initial and final particle sizes were 3.86μm and 4.67μm respectively, which were also the lowest. According to Stoke's Law, the sedimentation rate is expected to decrease with decreasing particle size, so the stability of DWG suspension with fraction 4 was the best. These results showed that a larger molecular weight of CLS could increase the

suspension stability. However, the sediment thickness, and the initial and final particle size of the DWG suspension with fraction 5 was larger than that with fraction 4. Obviously, the stability of suspension decreased when the molecular weight was too large. On the other hand, during the measuring period the growth of particle size decreased with rising molecular weight of CLS. It seemed that the steric stabilization effects that rose with rising molecular weight could reduce the particles aggregation and increase in size.

Suspending Ratio and Stability of DWG Suspension with LS Prepared with Different Cations

Some researchers have been concerned that LS with different cations could change its performance in various applications. Liu et al. (1997) found that the kind of cation of LS could influence the effects of the LS as water reducer, flowability, setting time of cement paste, and strength of hydrated cement. In this part different cation LS, Na-LS, Mg-LS, and Fe-LS acquired by ion-exchange from CLS, were used as dispersants for producing DWG, and the suspending ratios were also tested.
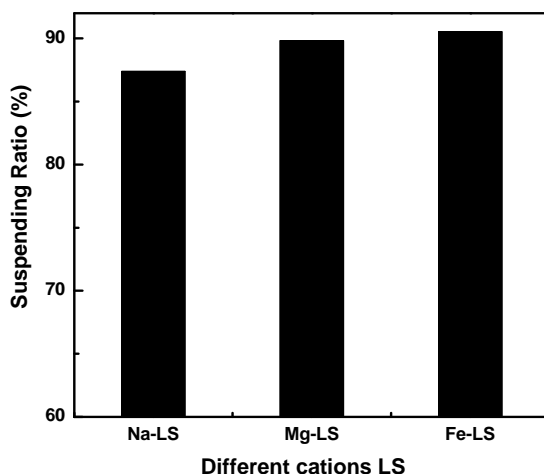

Fig. 4. Suspending ratio of DWG using different cation LS as dispersants

It can be seen from Fig. 4 that the suspending ratio had a slight increase with increasing valence of the cation. LS would dissociated into anions and corresponding cation in aqueous solution. The higher valence cation could increase the adsorbed amount of LS on the pesticide surface because it could reduce the molecular electrostatic repulsive forces of LS and increase the density of the adsorbed layer (Zhu and Gu 1991). Thus, the effectiveness of LS as a dispersant was enhanced with increasing valence of the cation.

Table 2. Stability of DWG Suspension with Different Cation LS

Suspension with different cation LS	Sediment thickness /mm	Initial particle size /μm	Final particle size /μm	Particle size growth /μm
Na-LS	0.40	3.83	4.89	1.06
Mg-LS	0.41	3.88	4.80	0.92
Fe-LS	0.40	3.48	4.51	1.03

The stabilities of DWG suspensions with LS having different cations were also investigated. The sediment thickness and particles size variation in the suspensions with different cation were acquired, and the results were listed in Table 2.

As displayed in Table 2, after 60 minutes the sediment thickness of these suspensions ranged from 0.40mm to 0.41mm, and the final particles size varied from 4.51μm to 4.89μm, which were much closer to each other. The particle size growths were all about 1.0μm. This meant that these suspensions were similar in stability, suggesting that the cation didn't influence the stability of the suspensions effectively.

Suspending Ratio of DWG with Different Degree of Sulfonation and Molecular Weight LS

Modified products of SLS (LS1~LS5) with similar molecular weight and different degree of sulfonation were acquired by changing the amount of Na_2SO_3, as listed in Table 3. The values of $[\eta]$ of LS1 ~ LS5 were close to 7.0 ml/g, while the degree of sulfonation varied from 1.58mmol/g to 1.81mmol/g. They were used as dispersants to produce DWG, and the suspending ratios of DWG were measured. As shown in Fig. 5, the suspending ratios of DWG increased with increasing degree of sulfonation. This means that the effectiveness of LS as a dispersant increased with rising degree of sulfonation when their molecular weights were similar. The reason was that the electrostatic effects increased with rising degree of sulfonation of LS, which helped to decrease the aggregation of particles more effectively.

Table 3. Modified Products of SLS with Different Intrinsic Viscosity and Degree of Sulfonation

Products	$[\eta]$ (ml/g)	Degree of Sulfonation (mmol/g)
LS1	6.84	1.58
LS2	6.54	1.66
LS3	6.89	1.69
LS4	7.28	1.75
LS5	6.83	1.81
LS6	6.04	1.75
LS7	6.80	1.75
LS8	7.78	1.75
LS9	10.23	1.75
LS10	13.49	1.75

Zhou et al. (2006) had found that the degree of sulfonation of different fraction of LS separated by ultrafiltration decreased with increasing molecular weight. The effectiveness of LS fractions as a dispersant might be mainly decided by its degree of sulfonation when its molecular weight was low, and so the suspending ratio of DWG decreased with decreasing molecular weight when the molecular weight of ultrafiltrated fraction of LS was below 10,000.
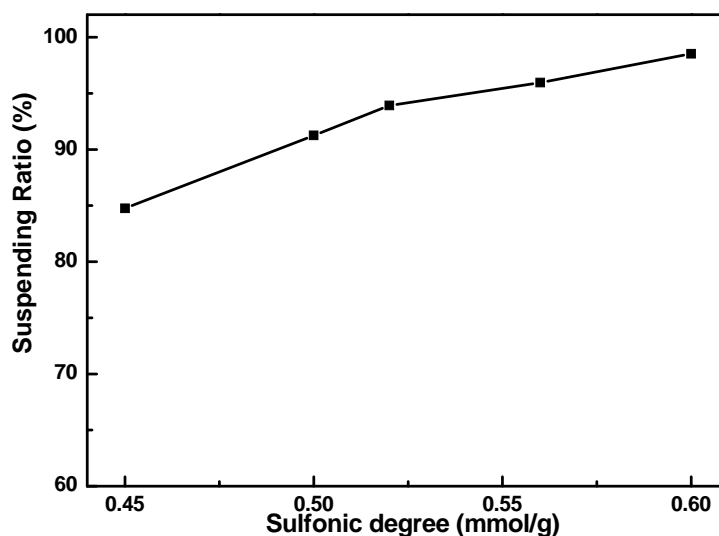
Fig. 5. Suspending ratio of DWG versus degree of sulfonation using LS1 ~ LS5 as dispersants

Modified products of SLS (LS6~LS10) with different molecular weight and the same degree of sulfonation were also acquired by changing the amount of formaldehyde. As shown in Table 3, LS6 through LS10 had different values of $[\eta]$ and the same degree of sulfonation of 1.75mmol/g. They were used as dispersants to produce DWG. Figure 6 shows that the suspending ratios of these five DWG increased with increasing $[\eta]$ at first, and when $[\eta]$ was larger than 7.78ml/g, the suspending ratio decreased slightly with increasing $[\eta]$. This was attributed to experimental errors. These findings further confirmed that the effectiveness of LS as a dispersant increased with increasing molecular weight.
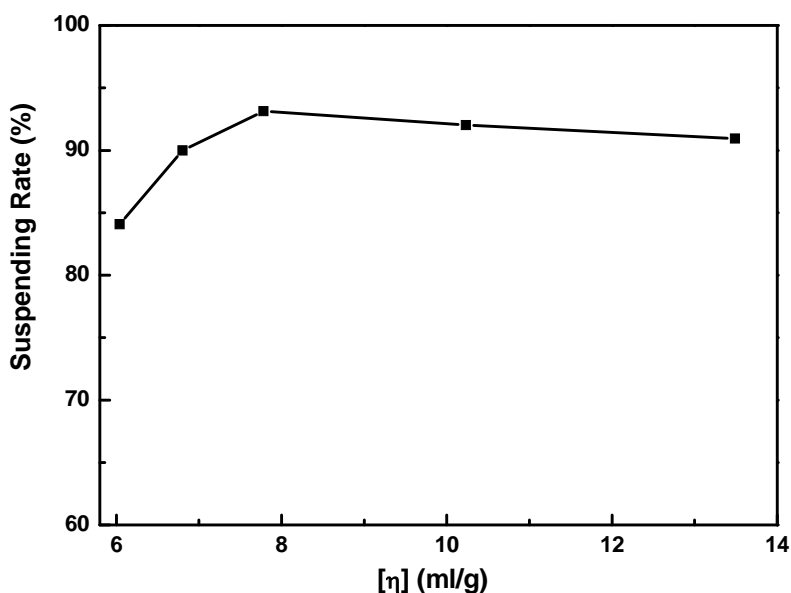

Fig. 6. Suspending ratio of DWG versus the value of $[\eta]$ using LS6 ~ LS10 as dispersant

By comparing Fig. 5 and Fig. 6, the suspending ratio of DWG increased from 84.71% to 98.51% when the degree of sulfonation of LS was varied from 1.58mmol/g to 1.81mmol/g, while it increased from 84.09% to 93.13% when the [η] of LS was varied from 6.04ml/g to 13.49 ml/g. This suggests that the degree of sulfonation contributed much more to the effectiveness of LS as a dispersant than the molecular weight.

Stability of DWG Suspension Using Different Degree of Sulfonation and Molecular Weight LS

The stability of DWG suspensions prepared with modified products of LS with different degree of sulfonation and molecular weight were measured using the Turbiscan LabExpert. The sediment thickness, the initial and final particle size, and the particle size variation of these suspensions were acquired. The results are listed in Table 4.

From Table 3, LS1, LS4, and LS5 had the same [η] and increasing degree of sulfonation. As shown in Table 4, during the 60 minute measuring period the initial particle sizes of these suspensions were close to each other. In the suspension with LS5 the final particle size was 4.05μm, which was smaller than the suspension with LS1 or LS4, and also the particle size growth in the suspension with LS5 was smaller than the other two. Also, the final particle size of the suspension with LS4 was smaller than that with LS1, as was the particle size growth. The stability of the suspension increased with increasing degree of sulfonation when LS had similar values of [η]. Obviously, the stability of the DWG suspension with LS5 was the best, suggesting that the stability of suspension was positively correlated with the effectiveness of LS as a dispersant.

Table 4. Stability of DWG Suspensions with Different Degree of Sulfonation and Molecular Weight of LS

Suspension with different LS	Sediment thickness /mm	Initial particle size /μm	Final particle size /μm	Particle size growth /μm
LS1	0.44	3.33	4.22	0.89
LS4	0.42	3.30	4.15	0.85
LS5	0.42	3.33	4.05	0.72
LS6	0.62	3.53	4.68	1.15
LS8	0.48	3.20	3.73	0.53
LS9	0.49	3.28	4.13	0.85
LS10	0.78	3.33	4.15	0.82

As displayed in Table 4, among the suspensions with LS6 and LS8 through LS10 (which had the same degree of sulfonation and increasing [η]), the particle size variation of the suspension with LS8 increased from 3.20μm to 3.73μm during the measuring period of 60 minutes, and the particle size growth of suspension with LS8 was only 0.53μm, which was smaller than the suspension with LS6, LS9, or LS10. Also the sediment thickness of the suspension with LS8 was only 0.48mm, which was the lowest among the four suspensions. So the suspension with LS8 had the best stability. It also could be seen from Table 4 that the stability of suspension increased with increasing values of [η] when [η] was in a suitable range and the degree of sulfonation was similar. It was further certified that the stability of suspensions was positively correlated with the effectiveness of LS as a dispersant.

CONCLUSIONS

1. Effects of molecular weight of calcium lignosulfonates (CLS) on their effectiveness as dispersants and the stability of suspension were investigated by using different ultrafiltrated fractions of CLS as dispersants for producing DWG. Larger molecular weight could improve the effectiveness as a dispersant of CLS and improve the stability of suspensions when it was in a suitable range. It was also found that larger molecular weight can reduce the growth of particles size more effectively.
2. Furthermore, effects of cations on the effectiveness of LS as a dispersant and the stability of suspensions were explored. The suspending ratio of DWG with Fe-LS was a little higher than with Na-LS and Mg-LS. The sediment thickness and particle size variation in these suspensions with different cation LS were close to each other, suggesting that cation didn't affect the effectiveness of LS as a dispersant and stability of suspensions distinctly.
3. Modified products of SLS having different degree of sulfonation and intrinsic viscosity were synthesized. The products were used as dispersants to produce DWG. The suspending ratio and suspension stability of the DWG were tested in order to illuminate how the degree of sulfonation and molecular weight of LS are likely to impact its performance in various applications. The results indicated that the higher the degree of sulfonation of LS, the better was the effectiveness of LS as a dispersant. When the molecular weight increased in a suitable range, the effectiveness of LS as a dispersant increased. The stability of DWG suspension was positively correlated with the effectiveness of LS as a dispersant.

ACKNOWLEDGMENTS

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