

Effects of Lignosulfonate Structure on the Surface Activity and Wettability to a Hydrophobic Powder

Yuanyuan Ge, Dingwei Li, and Zhili Li*

The wettability of a solid material is very important in many applications, such as food, agrochemical formulations, and cosmetics. Wettability can be improved by adding surface active agents, especially biocompatible surfactants derived from biomass. In this work, the surface activity (ability to lower the surface tension of an aqueous solution) and wettability toward a hydrophobic powder by a series of sodium lignosulfonates (NaLS) synthesized with different degree of sulfonation (Q_s) and weight-average molecular weights (M_w) were investigated by measuring the surface tension and contact angle. The results demonstrated NaLS with a larger M_w or lower Q_s had higher surface activity. Conversely, the wettability of the NaLS aqueous solution toward difenoconazole powder showed a reverse trend, *i.e.*, NaLS with a smaller M_w or higher Q_s improved the wettability to difenoconazole. The surface activity and wettability was controlled by the varying densities of the NaLS molecules at the water to air interface or the solid/liquid interface, which was dependent on the molecular structure of NaLS.

Keywords: Surface activity; Wettability; Lignosulfonate; Surfactant

Contact information: School of Chemistry and Chemical Engineering, Guangxi University, Nanning, 530004, China; *Corresponding author: lizhili@gxu.edu.cn

INTRODUCTION

When considering the properties of the final product, the wettability of a solid material is important in many technologies, such as pharmaceuticals, agrochemical formulations, flotation, and cosmetics (Sigal *et al.* 1998; Ferreira *et al.* 2007). Wettability is important for the disintegration, spread, and dissolving of solid granular forms, such as water-dispersible granulations. Because wetting is the pre-stage of dissolving, the wettability of hydrophobic particles strongly influences the dissolving and spreading rates and therefore often needs to be controlled (Lee *et al.* 2013). Commonly, wettability improvements of hydrophobic particles can be achieved by adding surface active agents into the formulations (Zdziennicka *et al.* 2003; Szymczyk and Janczuk 2007; Dobbelin *et al.* 2008).

Sodium lignosulfonate (NaLS), a byproduct of wood pulp manufacturing (Prasetyo *et al.* 2010), is a biocompatible surfactant that is widely used as an additive to control the stability and rheological properties of dispersing systems. Examples of various industrial applications include cement (Bishop and Barron 2006), coal-water slurry (Degtyarenko *et al.* 1988), textile dyeing (Dilling 1987), agrochemicals (Li *et al.* 2009; Li *et al.* 2011), and oil recovery (Gogoi 2011). These industrial utilizations of NaLS are closely related to its interaction with particles/droplets in dispersing systems. When NaLS is added to a dispersing system, it can be adsorbed onto the particle/droplet surface and cause the surface to become charged by the ionized sulfonic groups of NaLS (Askvik *et al.* 2001), which

may result in the formation of steric and electrostatic repulsive forces. The NaLS stabilizing mechanisms for particles were previously discussed in earlier publications by the authors (Li *et al.* 2012; Ge *et al.* 2013). The results of the previous studies revealed that the degree of sulfonation and the molecular weight of NaLS played an important role in the stabilization of agrochemical formulations.

The relationships between the molecular structure of NaLS and the wettability to a hydrophobic powder were, however, not clear. This information may be very helpful for the selection of surfactants to enhance the applied performances of agrochemical formulations, such as fast disintegration and spreading to form well-dispersed suspensions. Thus, the main objective of this work was to evaluate the surface activity (ability to lower the surface tension of an aqueous solution) and wettability toward a hydrophobic agrochemical by NaLS with different molecular weights and degree of sulfonation. This will provide a possible way to better understand the relationship between the molecular structure of NaLS and the wettability to a hydrophobic agrochemical powder.

EXPERIMENTAL

Materials

Sodium lignosulfonate batches (NaLS-1, NaLS-2, NaLS-3, and NaLS-4) were prepared from alkaline lignin with variable dosages of formaldehyde and Na₂SO₃ by a three-step method as follows (Li *et al.* 2011). First, alkaline lignin and 100 mL of distilled water were poured into a flask equipped with an electric heating device, a motor stirrer, a thermometer, a dropping funnel, and a reflux condenser. The mixture was heated to 50 °C for 30 min. A solution of NaOH was then used to adjust the pH of the solution to 10. Subsequently, hydrogen peroxide (60%, 0.08 g/g lignin) was added dropwise to pre-oxidize the lignin. After the reaction was maintained for 30 min, formaldehyde (37% 0.1 to 0.2 g/g lignin) was added dropwise, and hydroxymethylation maintained for 1 h. Second, the solution was heated to 85 °C, and Na₂SO₃ was added (0.35 to 0.76 g/g lignin) to cause sulfonation for 2 h. Finally, additional formaldehyde (37%, 0.05 to 0.15 g/g lignin) was added dropwise to copolymerize with the sulfonated lignin for 2 h. The reaction mixture was cooled to ambient temperature and then filtered with a hollow fibre membrane, which had a 2000-molecular weight cut off to remove inorganic reagent and low molecular organic residues.

The products were vacuum-dried at 60 °C overnight to yield brown powders. The prepared lignosulfonates have various favorable aspects including being derived from biomass, being widely available, adding value to an underutilized resources, being environmental friendly and biodegradability, among others.

Difenoconazole (C₁₉H₁₇Cl₂N₃O₃, CAS No. 119446-68-3) is a broad-spectrum fungicide used for disease control in many fruits, vegetables, cereals, and other field crops (Utture *et al.* 2011; Pinto *et al.* 2012). It was purchased from Sigma-Aldrich (USA) as an off-white, fine powder of analytical standard grade (99%). The powders were finely crushed to a mean particle size of 16.0 μm with irregular shapes for the determination of contact angle. Analytically pure *n*-hexane was obtained from Chengdu Union Chemical Industry Reagent Research Institute (China).

Methods

Characterization

The Fourier transform infrared (FT-IR) spectra of NaLS samples were obtained from an FT-IR spectrophotometer (Bruker Vector 33, Esslingen, Germany) using the KBr slice method. The degree of sulfonation of NaLS (Q_s) values were measured by chemical titration (809 Titrando, Metrohm Corp, Switzerland) (Wang 2002). The weight- and number-average molecular mass (M_w and M_n) and polydispersity (PD) of NaLS were measured by gel permeation chromatography using an Agilent 1100 GPC (USA) equipped with an auto sampler, an isocratic pump, a thermostat column compartment, and a multiple-wavelength detector. Tetrahydrofuran, HPLC-grade, was used as a solvent and eluent. Polystyrene was used as a standard (Sigma-Aldrich, USA).

Surface tension measurement

In this study, the surface tension (γ) of NaLS aqueous solutions with various concentrations were measured at 25 °C using the Wilhelmy plate method (Lee and Hildemann 2014) with a thermostat-controlled tensiometer (DCAT 11, DataPhysics Instruments GmbH, Germany). A thin, small plate made of platinum, which hangs on the balance, can measure the equilibrium surface tension of the aqueous solution at the air-liquid interface.

Contact angle measurement

Solid-liquid contact angle (CA) is defined as the angle made between the liquid-vapor surface and liquid-solid surface along a three-phase contact line (with the angle measurement within the liquid phase). Low CA implies that the liquid wets the surface and will spread readily across it, whereas a high CA implies that the liquid does not wet the surface and tends to form beads (Bayramoglu and Arica 2005). The common direct measurement of contact angles of a liquid drop on a flat and smooth solid is not applicable to powders and porous materials. The widely used method of measuring the contact angle of powder and porous materials is through a capillary rise method by using the Washburn equation (Kirdponpattara *et al.* 2013),

$$h^2 = \frac{r\gamma \cos \theta}{2\eta} t \quad (1)$$

where θ is the contact angle of the liquid on the solid (°), h is the height of the rising liquid, γ is the surface tension of the tested liquid (N/m), r is the mean static radius of the pores (m), and η is the liquid viscosity (Pa s).

The Washburn equation (1) presents linear dependence of square of the height penetration of penetrating liquid in the capillaries versus time. It was proposed to get the actual constant term r in Washburn equation by plotting the measured value $r\cos\theta$ versus the rate of rise of N-hexane, which is considered completely wetting, due to its low surface tension (Debbabi *et al.* 2008). After finding r , which is a property of the solid sample and does not change as a function of the liquids used, one then can conduct capillary rise experiments with a test liquid and calculate the contact angles this liquid creates with the powder sample.

Therefore, in this work, CA was measured by the capillary rise method to characterize the wettability of difeniconazole powders by NaLS aqueous solutions. Tests were carried out with a DCAT 11 contact angle meter from DataPhysics Instruments GmbH,

Germany). A fixed amount of powder was packed in a closed tube (7 mm internal diameter and 15 cm height) containing a frit on the bottom bed, which was treated like a capillary bundle. The tube was brought into contact with a liquid at the frit end. Driven by the capillary pressure, the liquid rose through the glass frit into the powder. The wetting behavior was analyzed by measuring the increase in mass of the liquid as a function of time using the Washburn equation (1). To maintain a constant powder density during the measurements, 1.5 g of powder was placed into the tube, which was then vibrated manually until the powder bed height reached 10 cm and the porosity was 72.13%.

RESULTS AND DISCUSSION

Structural Properties of Lignosulfonates

The FT-IR spectra of the samples are shown in Fig. 1. The peaks at 2850 and 2930 cm^{-1} can be attributed to the C-H stretching of methyl and methylene groups present in NaLS. The peaks observed at 1610, 1512, and 1420 cm^{-1} are from the aromatic skeletal vibrations of the NaLS samples (Hergert 1971). The other typical peaks found include: C-H asymmetric deformations at 1465 cm^{-1} , syringyl ring breathing with C-O stretching at 1330 cm^{-1} , guaiacyl ring breathing with C-O stretching at 1205 cm^{-1} , C-H in-plane deformation in guaiacyl and syringyl at 1120 cm^{-1} , O-H stretching at 3410 cm^{-1} , $-\text{SO}_3$ stretching at 1040 cm^{-1} , and aromatic C-H deformation at 850 cm^{-1} (Tejado *et al.* 2007). These data confirm the identical structural features of the NaLS samples.

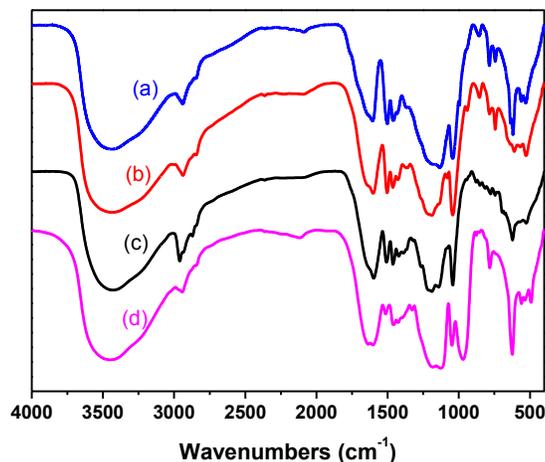


Fig. 1. FT-IR spectra of different sodium lignosulfonates (NaLS): (a) NaLS-1; (b) NaLS-2; (c) NaLS-3; and (d) NaLS-4

Table 1. Physical Characterizations of Different Sodium Lignosulfonates

NaLS	Q_s (mmol/g)	M_w	M_n	PD
Lignin	-	2561	657	3.89
NaLS-1	1.26	3638	913	3.98
NaLS-2	1.29	6423	1625	3.95
NaLS-3	2.29	4861	1356	3.58
NaLS-4	3.28	4956	1439	3.44

The Q_S , M_w , M_n , and PD of the NaLS and the original lignin were measured, and the results are tabulated in Table 1. Samples NaLS-1 and NaLS-2 have similar Q_S values (1.26 and 1.29 mmol/g, respectively) while having different M_w (3638 and 6423, respectively). Samples NaLS-3 and NaLS-4 have similar M_w (4861 and 4956, respectively) but have different Q_S (2.29 and 3.28 mmol/g, respectively). The PD values were all similar.

Surface Activity of NaLS

The surface activities of NaLS with different structural features were estimated by measuring their surface tension (γ) against the concentration of NaLS (Fig. 2). As expected, γ was dependent on the NaLS concentration, *i.e.*, as the concentration of NaLS increased, γ decreased until a plateau was reached.

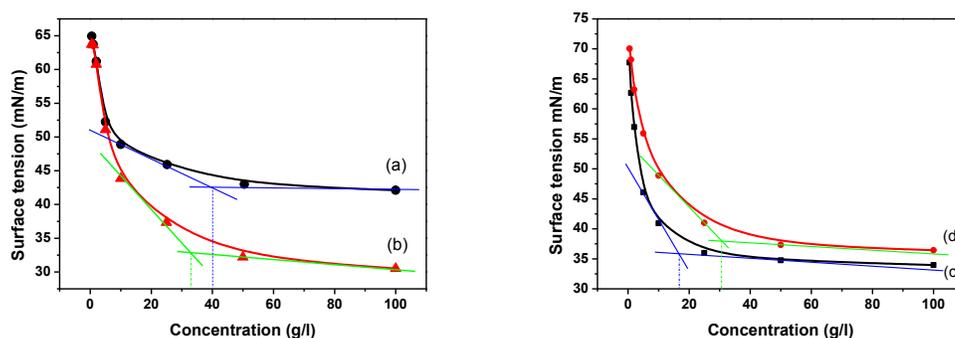


Fig. 2. Plots of surface tension to concentration of the sodium lignosulfonate solutions: (a) NaLS-1; (b) NaLS-2; (c) NaLS-3; and (d) NaLS-4

It is well known that there is a correlation between surface tension and concentration (Lee and Hildemann 2014), which is associated with the formation of supramolecular aggregates (namely, the critical micelle concentration (CMC) in the case of a surfactant, or the critical association concentration (CAC) in the case of a polyelectrolyte). The inflection point observed in Fig. 2a corresponds to the CAC values for NaLS-1 and NaLS-2, *i.e.*, 40.06 and 33.36 g/L, respectively. The inflection point demonstrates that increasing M_w (*i.e.*, hydrocarbon cluster) leads to decreasing CAC values, as generally found within other surfactant aqueous solutions (Debbabi *et al.* 2008). An examination of the data obtained (Table 2) shows a distinct increase in CAC with increasing Q_S , as indicated by comparing NaLS-3 (16.7 g/L) and NaLS-4 (30.57 g/L). The CAC and γ_{CAC} results are consistent with the hydrophobic domain being the predominant driving force for surfactant molecule aggregation in aqueous solution. When the NaLS contains more hydrocarbon clusters, for instance NaLS-2 ($M_w = 6423$), the hydrophobicity and the attracting force between molecules is much stronger, which results in an increasing surfactant aggregation density at the gas-liquid interface and in the micelles and therefore lower CAC and γ_{CAC} , *i.e.*, a higher surface activity can be obtained. Conversely, when the NaLS contains more sulfonic groups, for instance NaLS-4 ($S = 3.28$ mmol/g), the hydrophobicity and the electrostatic repulsive force between molecules is much stronger, which results in a decreasing surfactant aggregation density at the gas-liquid interface and in the micelles and therefore a higher CAC and γ_{CAC} , namely a lower surface activity.

The maximum surface concentration of NaLS at the gas-liquid interface (Γ) and the average surface area occupied by each NaLS molecule (\AA^2) can be calculated from the slope of the linear portion of curves obtained by plotting γ against $\log[C]$ and using the simplified Gibbs equation (Debbabi *et al.* 2008):

$$d\gamma = -2.303RTT d\log[C] \quad (2)$$

The quantity Γ can be directly calculated from the slope of $d\gamma/d\log[C]$, and the surface area occupied by each molecule is approximately $1/N\Gamma$, where N is Avogadro's constant (Adamson 1982). The results are tabulated in Table 2. Concerning the occupied surface area (\AA^2), which provides valuable information on the orientation of the molecules at the surface, the results obtained show a decrease of the surface area with increasing M_w ; for instance, NaLS-1 has a surface area of 190 \AA^2 , while that of NaLS-2 is 106 \AA^2 . Surface area also decreased with decreasing Q_s ; for instance, NaLS-4 exhibited a surface area of 116 \AA^2 , while that of NaLS-3 was 111 \AA^2 . The small area covered by the adsorbed NaLS reveals that the hydrophobic chains were closely packed at the gas-liquid interface. The results strongly confirm the aforementioned analysis.

Table 2. Values of the Critical Association Concentration (CAC), Surface Tension above CAC (γ_{CAC}), Surface Excess (Γ), Occupied Surface Area (\AA^2), and Contact Angle (CA) of Difenoconazole with NaLS Aqueous Solution

NaLS	CAC (g/L)	γ_{CAC} (mN/m)	Γ (10^{-10} mol/cm 2)	Area (\AA^2)	CA ($^\circ$)
NaLS-1	40.06	42.1	0.95	190	69.9
NaLS-2	33.36	32.5	1.56	106	72.8
NaLS-3	16.72	35.7	1.48	111	77.1
NaLS-4	30.57	38.2	1.32	116	73.2

Influence of Molecular Structure of Lignosulfonates on the Wettability

The CA was measured to evaluate the wettability of different NaLS aqueous solutions toward difenoconazole powder, and the results are shown in Fig. 3. The results demonstrate a strong CA-concentration relationship. As the concentration of NaLS increased, the CA decreased *i.e.*, the wettability of difenoconazole powders increased. Similarly, as the concentration increased, the γ decreased (Fig. 2), which allowed the liquid to easily penetrate into the capillary spaces of the powders, resulting in a CA decrease.

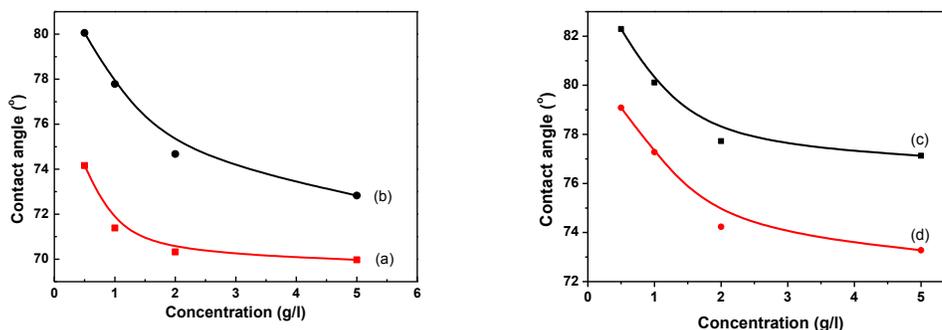


Fig. 3. Plots of contact angle of difenoconazole powder with lignosulfonate solution at different concentrations: (a) NaLS-1; (b) NaLS-2; (c) NaLS-3; and (d) NaLS-4

It should be noted that different characteristics are present between the wettability of NaLS toward difenoconazole powder and the surface active properties of NaLS. That is, NaLS-2 and NaLS-3 have shown higher surface activities than NaLS-1 and NaLS-4 but have presented lower wettabilities toward difenoconazole powders (Fig. 3 and Table 2).

The current method for measuring contact angle is based on capillary pressure driving the liquid to penetrate the packed bed of powder until an equilibrium height of liquid is reached (Lazghab *et al.* 2005). Therefore, the rise of liquid into a capillary will be controlled by the competition of capillary pressure and attractive forces between aggregating NaLS molecules at the air-water interface (as shown in Fig. 4). That is, the interaction of NaLS molecules also plays a role in the capillary rise. As discussed in the previous sections, NaLS molecules with larger M_w (such as NaLS-2) will display strong van der Waals attraction between the molecules, resulting in a tight assembly at the air-water interface (lower \AA^2). Therefore, it is hard to overcome the strong attraction of NaLS molecules to make the liquid penetrate into the capillary in powders, which consequently results in poor wettability toward the powders (such as NaLS-2 compared to NaLS-1). Comparing NaLS-4 and NaLS-3, NaLS-4 showed a better wettability toward difenoconazole powder. This situation must be due to the strong electrostatic repulsive forces between NaLS molecules generated by sulfonic groups, which therefore causes the NaLS to easily penetrate into the capillary spaces in the powders.

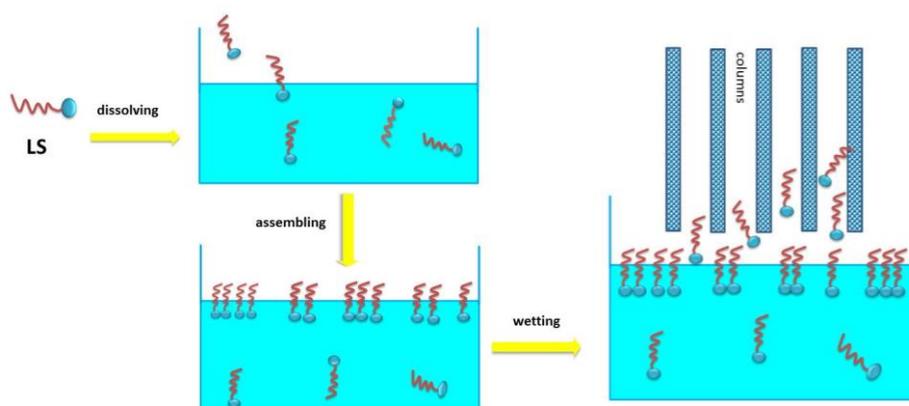


Fig. 4. Schematic illustrating the wetting of powders by LS

CONCLUSIONS

1. The surface activity and wettability of NaLS toward a hydrophobic powder were found to be dependent on its structural features. An inverse relationship was seen concerning the degree of sulfonation and weight-average molecular weight of NaLS.
2. The inverse relationship between the surface activity and wettability was because the assembling density of NaLS molecules at the water-air interface increased with increasing weight-average molecular weight but with decreasing degree of sulfonation, which therefore resulted in a lower surface tension, *i.e.*, higher surface activity. The higher assembling density of NaLS molecules can lead to stronger attractive forces, making it difficult for the liquid to penetrate into the capillary spaces in a powder that demonstrated higher contact angles, *i.e.*, poor wettability.
3. This study provides a possible method to better understand the relationship between the molecular structure of NaLS and the wettability toward a hydrophobic agrochemical powder. That is, NaLS with a lower weight-average molecular weight or a higher degree of sulfonation will provide a benefit for the wettability of a hydrophobic powder.

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