



Influence of molecular mass of lignosulfonates on the resulting surface charges of solid particles

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ABSTRACT

Different lignosulfonate (LS) samples were prepared via a three-step method and were characterized by FT-IR, UV, GPC and functional groups measurement. FT-IR and UV spectra confirmed the prepared samples had typical characteristics of lignin materials. GPC and functional groups measurement results indicated the samples had different molecular mass (M_w), but same quantities of sulfonic groups (S). The influence of M_w of LS on the resulting surface charges of dimethomorph particles via adsorption was further investigated. The results indicated that the adsorption isotherms of LS on dimethomorph surfaces belonged to L-type and the adsorption capacity (q_m) increased with increasing M_w . However, the non-linear correlation between zeta potentials with the products of S and adsorption amount (SA) indicated SA did not positively improve the surface charges expectedly. Based on the analysis, an adsorption confirmation was proposed allowing prediction of the relation between M_w and surface charge efficiency of LS for solid particles.

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1. Introduction

Nowadays, lignin based materials are receiving increased attentions because of their natural virtues of renewable bioresources [1–7]. Lignosulfonate (LS) is an important derivative of lignin and is composed of phenyl propane units with sulfonic groups, carboxylic acid groups and phenolic-OH groups, etc. [8,9], among which the sulfonic groups are the main hydrophilic functional groups contributing to its good water solubility. LS is frequently used as an additive to control the stability and rheological property of a dispersing system. Examples of varied industrial applications include cement [10], coal-water slurry [11], textile dyeing [12], agrochemicals [13], oil recovery [14], etc. Its wide industrial utilizations are closely related to the interaction of LS with particles/droplets. When LS is added to a dispersing system, it can be adsorbed onto the particles/droplets surface and following charged the surface by the ionized sulfonic groups [15]. The surface charge is commonly evaluated by the magnitude of zeta potentials [16]. As a result, the dispersing systems can be stabilized by repulsive forces through the electrical double layers between particles/droplets. This characteristic behavior can be interpreted definitely by the theory of DLVO [17,18].

Due to the structural complexity of LS macromolecule, its solution behavior in aqueous system is not very clearly yet. The expanding utilization of LS needs a better understanding of the correlations between structural features of LS and its applied performance. Especially, the adsorption behavior of LS on particles/droplets surface and subsequent the surface charges are essential in determining the electrostatic repulsive forces between particles/droplets which thoroughly affect the dispersion and stability of dispersing systems.

In this study, LS samples with different molecular mass but same quantity of sulfonic groups were prepared via a three-step method. The adsorption behaviors of the LS samples on dimethomorph surface were further investigated. This study especially focused on how the molecular mass of LS influenced the resulting surface charges of solid particles via adsorption. Based on the results obtained in this work, a physical adsorption model was regressed allowing prediction of the structure characteristics and surface charge efficiency of LS.

2. Materials and methods

2.1. Materials

Dimethomorph ($C_{21}H_{22}ClNO_4$) [19], a systemic morpholine fungicide, was used as a solid adsorbent being provided as a light white powder by Jiangsu Frey Agrochemicals Ltd., China. It was washed twice in distilled water for 10 min and then filtered to

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remove organic contaminants before utilization. Its basic properties were described in our previous work [20].

LS samples were prepared from an alkaline lignin, derived from wheat straw via alkaline pulping (Quan Lin Zhiye Co., Ltd., China) by a three-step method including oxidation, hydroxymethylation, sulfonation and copolymerization [21]: (i) A certain amount of raw lignin and 100 mL distilled water was poured into a flask bottle 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 and some sodium hydroxide was added to adjust pH to 10. Subsequently, hydrogen peroxide was added dropwise to pre-oxidize lignin. The reaction was maintained 30 min and then formaldehyde was added for hydroxymethylation for 1 h. (ii) The solution was heated to 85 °C and an amount of Na₂SO₃ with a ratio of 0.49 to lignin was added for sulfonation for 2 h. (iii) Finally another part of formaldehyde was added to copolymerize with sulfonated lignin for 2 h. The total amounts of formaldehyde were within the ratios of 0.04–0.12 to lignin. The reaction products were purified by ultrafiltration with a hollow fiber membrane, which had a 1000 molecular mass cut off to remove the inorganic reagent residues and other organics. The cut fraction products were vacuum dried at 60 °C overnight to yield brown powders. By adjusting the reaction parameters, a serial lignosulfonates were prepared, named with *a*, *b*, and *c*, respectively.

2.2. Characterizations

FT-IR spectroscopy was often used to characterize lignin and lignin derivatives [22]. In this study, FT-IR spectra of LS samples were obtained from an FT-IR spectrophotometer (Bruker Vector 33, Esslingen, Germany). The scan region was between 4000 and 400 cm⁻¹. Each sample was prepared according to the potassium bromide slice method with a proportion of 1% to KBr.

The ultraviolet spectra of LS samples were investigated by an UV-2102PC spectrophotometer (UNICO (Shanghai) Instruments Co. Ltd., China). The scan was conducted between 200 nm and 400 nm wavelength.

The weight-/number-average molecular mass (M_w , M_n) and polydispersity (M_w/M_n) of LS samples were measured with an Agilent 1100 gel permeation chromatography (GPC). HPLC-grade tetrahydrofuran was used as solvent and eluent for the measurement. The column temperature was 50 °C. Polystyrene was used as standards (Sigma–Aldrich). The injection volume was 20 μL.

The quantities of sulfonic groups (*S*) of LS samples were measured by a potentiometric titration method (AT-510, KEM, Japan). LS samples were firstly transformed into lignosulfonic acids by passing through anion exchange resins and cation exchange resins which were based on crosslinked polystyrene and obtained from Lantian Chemicals, China in turn. A certain volume of lignosulfonic acid (V_1 , mL) solution was titrated with 0.01 M NaOH. The pH of the solution increased with increasing consumption of NaOH (V_2 , mL) until the differential curve showed a distinctive mutation. The concentration of lignosulfonic acid (C_1 , g L⁻¹) solution was determined by an UV spectrophotometer. The quantity of sulfonic groups was calculated by Eq. (1) [23]:

$$S(\text{mmol g}^{-1}) = \frac{0.01 \times V_2 \times 10^3}{V_1 \times C_1} \quad (1)$$

2.3. Adsorption experiment

The adsorption amount of LS on dimethomorph surface was determined as the difference between the concentrations of LS solutions before and after adsorption equilibrium. A fixed amount (m , g) of purified dimethomorph powder was added into a flask loading 50 mL LS aqueous solutions (V , mL) with a certain

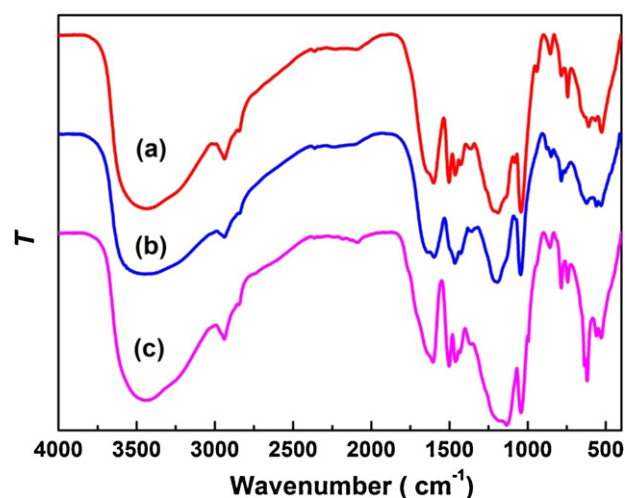


Fig. 1. FT-IR spectra of the different lignosulfonates (a; b; c).

concentration (C_0 , g L⁻¹) and then the mixture was shaken in a thermostatic bath at 30 °C for 5 h. After 24 h equilibration, the sample was centrifuged at 10,000 rpm until a clear supernatant was obtained (C_e , g L⁻¹). The experiment was conducted three times, if the relative standard deviation for any sample exceeded 5%, the measurement was repeated. The adsorption amount of LS on dimethomorph surface was expressed as Eq. (2):

$$\text{adsorption amount (mg g}^{-1}\text{)} = \frac{V(C_0 - C_e)}{m} \quad (2)$$

2.4. Zeta potentials measurement

Electrophoresis is widely used to examine the surface charges of particles which can be charged by themselves or other ions through adsorption [24]. The results are often represented by zeta potentials indicating the magnitude of charged strength [25]. In this section, zeta potentials of dimethomorph particles were determined as a function of concentration of LS. The aqueous suspensions containing 0.5 wt% dimethomorph powder and different LS dosage were prepared. The zeta potential measurement was conducted by means of an apparatus of Nano-S Zetasizer (Malvern Instruments Ltd., UK) at pH = 6.9. A syringe was used to deliver sample to the electrophoresis cell. The cell was washed by the sample suspension and then was injected in the fresh sample, followed by 1 min of equilibration. Each sample measurement consisted of three continuous tests. If the relative standard deviation for any sample exceeded 5%, the measurement was repeated.

3. Results and discussions

3.1. Physical–chemical properties of lignosulfonates

The FT-IR spectra of the prepared LS samples were shown in Fig. 1. The fingerprint region lied between wave numbers ranging from 700 cm⁻¹ to 1600 cm⁻¹ and typical stretching of chemical groups was observed at 2800 cm⁻¹ to 3500 cm⁻¹. The peaks at 2850 cm⁻¹ and 2930 cm⁻¹ were mainly attributed to the C–H stretching of methoxyl and methylene groups which presented much less differences. The peaks at 1610 cm⁻¹, 1512 cm⁻¹ and 1420 cm⁻¹ contributing to aromatic skeletal vibration were observed for the LS samples [26], which confirmed that the “core” of lignin structure did not change dramatically during the chemical procedures. The other typical peaks could also found in these curves: C–H asymmetric deformations at 1465 cm⁻¹, syringyl ring breathing with C–O stretching at 1330 cm⁻¹, guaiacyl ring

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