

## Adsorption Mechanism of Lignosulfonate at the Air/Liquid Interface

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Lignosulfonate is a type of natural polymer surfactant. Its capability to reduce the surface tension of aqueous solution depends on its adsorption configuration at the air/liquid interface. The dynamic surface tension, the air/liquid interfacial film properties of lignosulfonate at different solution concentrations, pH values and ionic strengths had been measured in the present work. The results showed that the adsorption equilibrium of lignosulfonate at the air/liquid cannot be achieved in a short period; the diffusion coefficient of lignosulfonate from the liquid to the air/liquid interface decreased with the increasing of pH value, while it increased with the increasing of ionic strength. Lignosulfonate could form soluble monomolecular film at the air/liquid interface, whereas the film was unstable. The stability of lignosulfonate monomolecular film became poor with the increasing of solution concentration, ionic strength and decreasing of pH value. Combining with our previous research results, the adsorption mechanism of lignosulfonate at the air/liquid interface was proposed.

**Keywords:** lignosulfonate, air/liquid interface, monomolecular soluble film

### Introduction

Surfactant molecules contain hydrophobic and hydrophilic groups. When surfactants are dispersed in water, the hydrophobic groups generally adsorb at the air/liquid interface; while the hydrophilic groups remain in the aqueous phase. The adsorption of surfactant molecule at the air/liquid interface leads the reduction of the surface tension of water; while the capability of a surfactant to reduce the surface tension of water is related to its arrangement configuration at the air/liquid interface, and the arrangement configuration depends on the surfactant concentration, pH value and ionic strength of solution, and etc.<sup>1,2</sup>

Lignin is a natural polymeric material that is only less than cellulose in amount, and it is one of the main pollution sources, which coming from waste water in the paper-making factory. Lignosulfonate is a by-product of acidic sulphite-pulping. Unlike lignin, lignosulfonate not only contains hydrophobic groups, such as aromatic and aliphatic groups, but also contains many hydrophilic groups, such as sulfonic, carboxyl and phenolic hydroxyl groups. It

is a natural polymeric surfactant that can be widely used as concrete water reducers,<sup>3,4</sup> coal water slurry dispersants,<sup>5-7</sup> oil-well dispersants<sup>8</sup> and pesticide dispersing agent.<sup>9</sup> But the surface activity of lignosulfonate is lower without chemical modification. The adsorption configuration of lignosulfonate at the air/liquid interface directly affects its surface activity, but so far there are few reports about the adsorption configuration of lignosulfonate at the air/liquid interface. Gundersen *et al.*<sup>10</sup> studied the adsorption process of lignosulfonate at the air/liquid interface by Langmuir technique. Their results showed that the concentration of lignosulfonate, pH value and ionic strength of solution affected the adsorption configuration of lignosulfonate at the air/liquid interface, but the researchers did not conclude about in what configuration lignosulfonate adsorbed at the air/liquid interface. Following our previous research,<sup>11</sup> we studied the influence of concentration of lignosulfonate, pH value and ionic strength on the dynamic surface tension and the air/liquid interfacial film properties of lignosulfonate solution, and the adsorption mechanism of lignosulfonate at the air/liquid interface was discussed.

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## Experimental

### Materials

Commercial sodium lignosulfonate is a by-product of the sulfite pulping process that is provided by Shixian Papermaking Co. Ltd.; which consists of about 70 wt.% of sodium lignosulfonate (SL), about 11 wt.% of reductive substance, and the rest are sugar acids, low molecular weight organic and inorganic salts. Before experiments, the commercial SL was purified by using filtration membrane, with a cut of molecular weight at 2500 Da. The operation was under a pressure of 0.42 MPa and a temperature of  $< 50\text{ }^{\circ}\text{C}$ . The mass average molecular weight ( $M_w$ ), the average number of molecular weight ( $M_n$ ), the polydispersity ( $M_w/M_n$ ) aqueous gel permeation chromatography (GPC) with a UV absorbance detector (Waters Corp., USA), and the content of main function groups of the purified SL (PSL) (an automatic potentiometric titrator (809 Titrator, Metrohm Corp.)) are listed in Table 1. Analytical grade sodium chloride, sodium hydroxide, hydrochloric acid and ethanol were purchased from Sigma-Aldrich (Shanghai, China), and used without further purification. Double distilled water was used for the preparation of all solutions.

### Dynamic surface tension measurements

The dynamic surface tension was measured by using a Wilhelmy plate with Dynamic Contact Angle meter from Dataphysics Instruments Co., Ltd. (Germany).

### The Langmuir technique

Surface pressure-area ( $\pi$ -A) isotherms were recorded with a prototype KSV 5000 Langmuir trough double-barrier system developed by KSV Chemicals (Helsinki, Finland). The trough and the barriers were made entirely of Delrin. Compression of the film was carried out with a barrier speed of  $3\text{ mm min}^{-1}$  per barrier. The stability of the PSL film at the air/liquid interface was evaluated by compressing the surface films to a fixed hold-value of  $6.0\text{ mN m}^{-1}$ . The film pressure was held constantly by continuously adjusting the film area (A),  $A_0$  is the starting area at the hold-value. The computer automatically recorded the change of  $A/A_0$  with time. In both surface pressure measurements, the trough the

trough and the barriers were cleaned by ethanol firstly, and then flushed by the de-ionized water. After that, the trough was filled with PSL solution and allowed the PSL molecules to adsorb for 30 min before the isotherms were recorded.

Hydrochloric acid and sodium hydroxide were used for pH adjustment. All experiment data in the present work were measured at 298 K.

## Results and Discussion

### Dynamic surface tension

Lignosulfonate is a surface-active component. It will adsorb to the air/liquid interface and build up an interfacial surface film, thus reducing the surface tension of the liquid. Dynamic surface tension is widely employed to investigate surfactant behavior and the adsorption of surfactant at the interface of liquid/liquid or air/liquid systems.<sup>12-14</sup> Figures 1, 2 and 3 show the dynamic surface tension curves of PSL obtained at different concentrations, pH values and ionic strengths, respectively. Figure 1 shows that the surface tension of PSL solution at three different concentrations reduces with the extension of time, which indicates that the adsorption of PSL at the air/liquid interface does not achieve equilibrium state in the measured range. The same result had also been reported by Li *et al.*,<sup>15</sup> the reason may be related to the adsorption behavior.

The adsorption of surfactant molecules at the air/liquid interface can be divided into two stages: (i) the dispersed

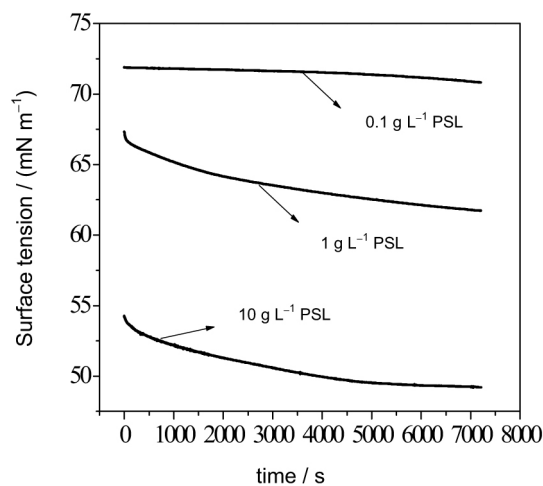
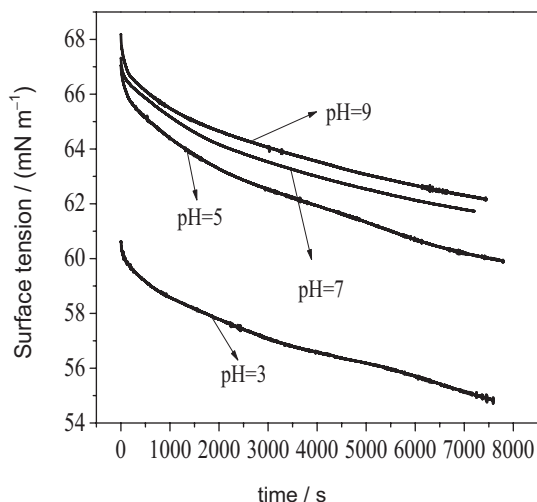


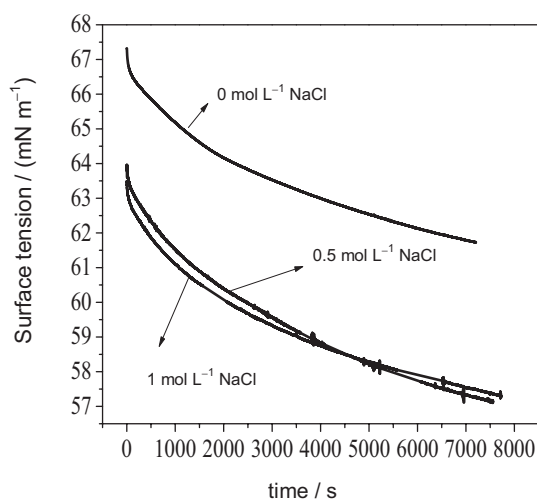
Figure 1. The  $\gamma$ -t curves of PSL with different concentrations.

Table 1. The molecular weight of PSL and the content of main functional groups in PSL

Sample	Molecular weight and polydispersity			Content of main functional groups		
	$M_w$	$M_n$	$M_w/M_n$	Sulfonic / wt. %	Carboxyl / wt. %	Phenolic hydroxyl / wt. %
PSL	13000	4900	2.7	11.34	6.57	1.86



**Figure 2.** The  $\gamma$ - $t$  curves of PSL at different pH values, the concentration of PSL is  $1 \text{ g L}^{-1}$ .



**Figure 3.** The  $\gamma$ - $t$  curves of PSL at different ionic strengths, the concentration of PSL is  $1 \text{ g L}^{-1}$ .

surfactant molecules spread from liquid phase to subsurface (the area close to the air/liquid interface); (ii) the surfactant molecules exchange between subsurface and the air/liquid interface, and adsorb at the air/liquid interface. The corresponding adsorption mechanism has two types of extreme cases: (i) the exchange of surfactant molecules between subsurface and the air/liquid interface completes instantaneous and the adsorption process is controlled by diffusion; (ii) the adsorption process is controlled by the exchange of surfactant molecules between subsurface and the air/liquid interface. The adsorption mechanism of macromolecular surfactant, which has longer chain branches with good flexible and the molecular chain tangles severely, cannot be explained simply by the above two extreme cases; but at the beginning of adsorption, the macromolecule surfactant will immediately adsorb at the air/liquid interface as long as they reach the subsurface;

in this situation, the potential barrier of adsorption can be nearly negligible and the adsorption process is controlled by diffusion; the diffusion rate of macromolecule surfactant from solution to the air/liquid interface can be expressed by the following equation:<sup>16</sup>

$$dn/dt = (D/\pi)^{1/2} C_0 t^{-1/2} (N_A/1000) \quad (1)$$

where  $C_0$  is the concentration of macromolecule surfactant in solution,  $n$  is the adsorption number of macromolecule surfactant *per* square centimeter at time  $t$ ,  $D$  is the surfactant molecular diffusion coefficient in the solution,  $\pi$  is the ratio of the circumference of a circle to its diameter and  $N_A$  is the Avogadro's number. After integral, equation 1 transforms to equation 2:

$$n = 2(D/\pi)^{1/2} C_0 t^{1/2} (N_A/1000) \quad (2)$$

Equation 2 indicates that  $n$  is proportional to the square root of  $D$  at the same time ( $t$ ) and under the same concentration ( $C_0$ ), which can be expressed as the following equation:

$$n \propto D^{1/2} \quad (3)$$

Based on the above analysis, when  $t$  approaches to zero, the PSL adsorption process is approximately controlled by diffusion. Figure 2 shows that the surface tension of PSL solution increases with the increasing of pH value when  $t$  approaches to zero; this result indicates that the number of PSL molecules adsorbing at the air/liquid interface *per* area unit decreases with the increasing of pH value. Based on equation 3, the conclusion can be presented that, when pH value increases, the diffusion coefficient  $D$  decreases. On the basis of our previous results,<sup>11</sup> the weakly ionized groups, such as carboxyl and phenolic hydroxyl, in PSL molecule ionize when the pH value increases, thus the cores of the PSL molecule expand as the pH value of the solution increases; and the hydrophobic chain of PSL stretches, which tangles each other in the solution and impedes the diffusion of PSL molecule; in addition, the weakly ionized groups ionize as pH value increases and the amount of hydrophilic groups in PSL molecule increases, thus the trend of PSL molecule from solution to the air/liquid interface is reduced, so the diffusion coefficient of PSL molecule decreases with the increasing of pH value.

PSL is a kind of anion surfactant, the change of ionic strength in solution will affect the electrostatic interaction between molecules, and then affect the adsorption behavior of PSL molecule at the air/liquid interface. Figure 3 shows the effect of ionic strength on the dynamic surface tension of

PSL. It can be seen that when  $t$  is close to zero, the surface tension of PSL solution under the same concentration decreases as the ionic strength increases, which means that the adsorption number of PSL molecule at the air/liquid interface *per* area unit increases with the ionic strength increase; it indicates that the diffusion coefficient  $D$  of PSL in solution increases as the ionic strength increases according to equation 3. As the ionic strength increases, the hydrophobic core of PSL molecule will become compact because of electrostatic shielding; thus the tangling of hydrophobic chain between PSL molecules in diffusion process decreases, and the diffusion coefficient  $D$  of PSL molecule increases as the ionic strength increases.

#### The properties of the air/liquid interfacial film

##### The $\pi$ -A curves

There are two types of monomolecular films at the air/liquid interface: (i) soluble substance diffuses from liquid to subsurface and adsorbs at the air/liquid interface to form soluble monomolecular film; and (ii) insoluble substance spreads at the air/liquid interface to form insoluble monomolecular film. During the formation of soluble monomolecular film, the hydrophobic parts of surfactants exposed to the air/liquid interface and the hydrophilic parts stay in liquid. If the double barriers compress the soluble film, a part of surfactant adsorption at the air/liquid will be against the osmotic pressure to return to the solution and keep balance between the solution and film. Langmuir technique uses two pieces of barriers with a speed of  $3 \text{ mm min}^{-1}$  *per* barrier to compress the film and records the surface pressure ( $\pi$ ) changes with the film area ( $A$ ); the  $\pi$ -A curve will help to understand the arrangement of PSL at the air/liquid interface.

The  $\pi$ -A curves of PSL at different concentrations, pH values and ionic strengths are shown in Figures 4, 5 and 6, respectively. In Figure 4, it can be seen that when the film area is larger, the surface pressure increases slowly as the barriers compress the film layer. This result indicates that the arrangement of PSL molecules at the air/liquid interface is loose; while the pressure increases significantly as the film area continues to decrease, which means that PSL molecules become more closely packed at the air/liquid interface. When the concentration of PSL is  $0.1 \text{ g L}^{-1}$ , there are a few of PSL molecules adsorbing at the air/liquid interface. Even as the barriers compress the film layer to smaller area, the arrangement of PSL molecules at the interface is still very loose, thus the change of surface pressure with barriers compressing is smaller.

Figure 5 shows the  $\pi$ -A curves of PSL at different pH values when the concentration of PSL is  $0.5 \text{ g L}^{-1}$ .

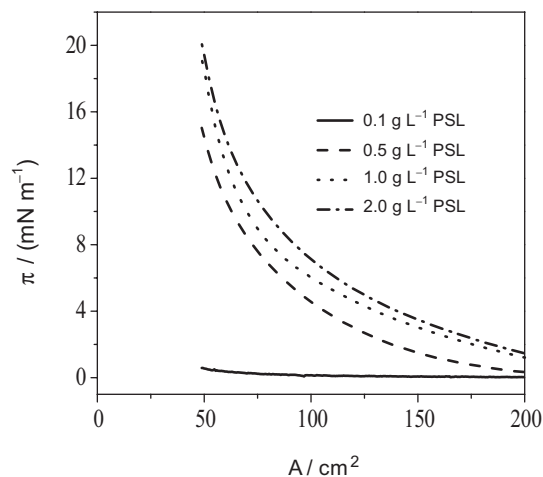


Figure 4. The  $\pi$ -A curves of PSL with different concentrations at pH 7.

The ionization of the carboxyl and phenolic hydroxyl groups will be suppressed in acidic solution, and the ionization of weak acidic functional groups will increase as the pH value of solution increases.<sup>11</sup> Due to the more hydrophobic character of PSL molecule and the stronger electrostatic repulsion coming from the intramolecules and intermolecules of PSL molecules at high pH value, fewer PSL molecules will adsorb to the air/liquid interface from an alkaline than an acidic solution, thus the surface pressure decreases as the pH value increases.

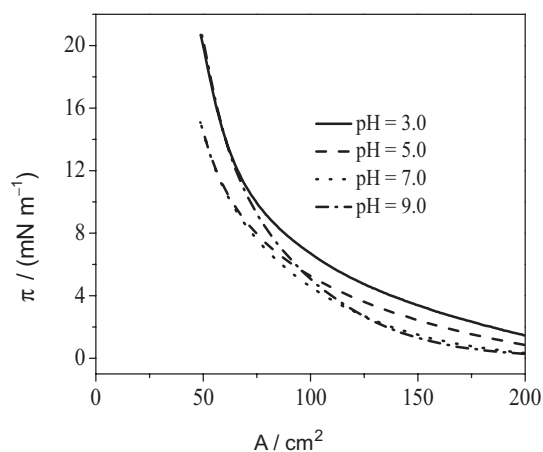
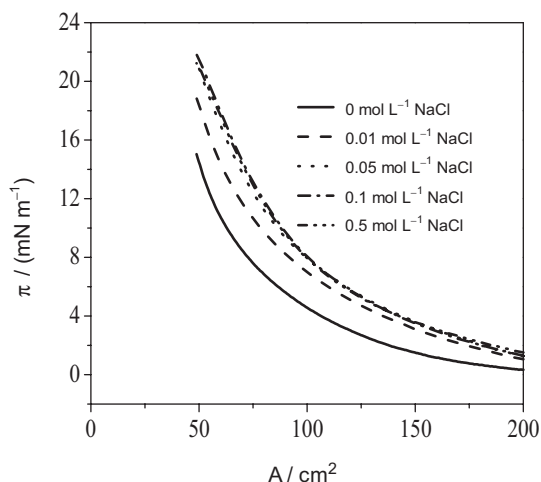


Figure 5. The  $\pi$ -A curves of PSL solution at different pH values, the concentration of PSL is  $0.5 \text{ g L}^{-1}$ .

In Figure 6, it can be observed that the surface pressure increases as the ionic strength increases, it implies that the arrangement of PSL molecules at the air/liquid becomes closer under higher ionic strength. There are ionized carboxyl and phenolic hydroxyl groups in the core of PSL molecule, the increasing of ionic strength will screen the electrostatic repulsion in the hydrophobic core of PSL molecule, so the core of PSL molecule will



**Figure 6.** The influence of ionic strength on the  $\pi$ - $A$  curves of PSL solution, the concentration of PSL is  $0.5 \text{ g L}^{-1}$ .

shrink, and the adsorption amount of PSL molecules at the air/liquid interface within area unit will increase, thus the surface pressure increases as the ionic strength increases. Figure 6 also shows that when the concentration of NaCl increases to  $0.05 \text{ mol L}^{-1}$ , the  $\pi$ - $A$  curves overlaps as the ionic strength increases. This result indicates that the arrangement configuration of PSL molecules at the air/liquid interface will not change when the ionic strength of solution increases to a certain degree.

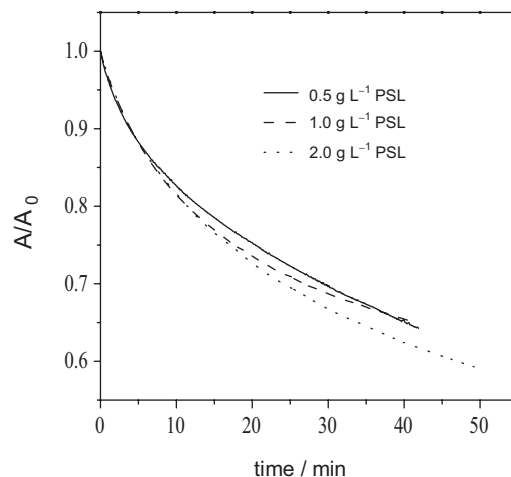
#### The stability of the air/liquid interfacial film

Unlike traditional insoluble Langmuir-films, which will collapse upon extensive compression, the PSL molecule will detach from the air/liquid interface and dissolve in solution during compression. This film property was evaluated by compressing the film to a fixed hold-value of  $6.0 \text{ mN m}^{-1}$ . The surface pressure was held constant by continuously adjusting the film area ( $A$ ). Figures 7, 8 and 9 show how the  $A/A_0$  ratio of PSL changes as a function of time under different concentrations, pH values and ionic strengths. The property of PSL film is more stable if the  $A/A_0$  ratio change smaller over time, otherwise the stability of PSL film is poor.

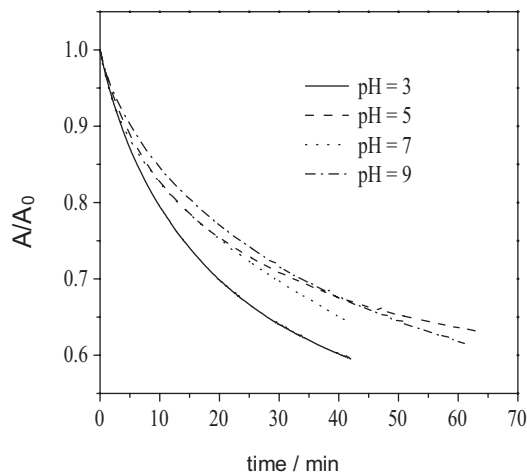
Figure 7 shows that the  $A/A_0$  ratio decreases as the time extends, which means that the PSL molecules breakaway from the film and dissolve in solution as time extends, so the barriers adjust the film area to keep the same surface pressure. In Figure 7, the decreasing level of  $A/A_0$  ratio increases slightly as concentration of PSL increases, which indicates that the PSL film is more unstable at higher concentrations.

Figures 8 and 9 show that the decreasing level of  $A/A_0$  ratio increases as the pH value decreases and ionic strength

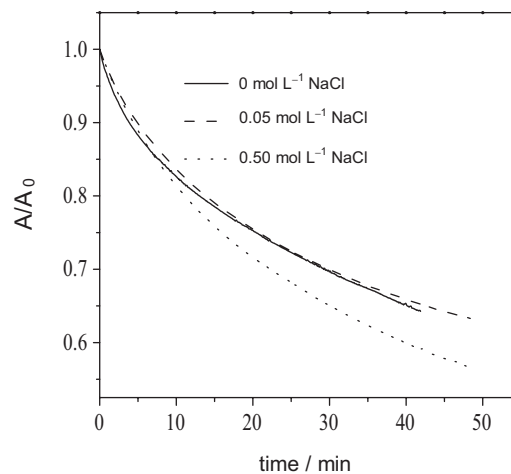
increases, respectively, indicating that the stability of the PSL film becomes poor at lower pH value and higher ionic strength.



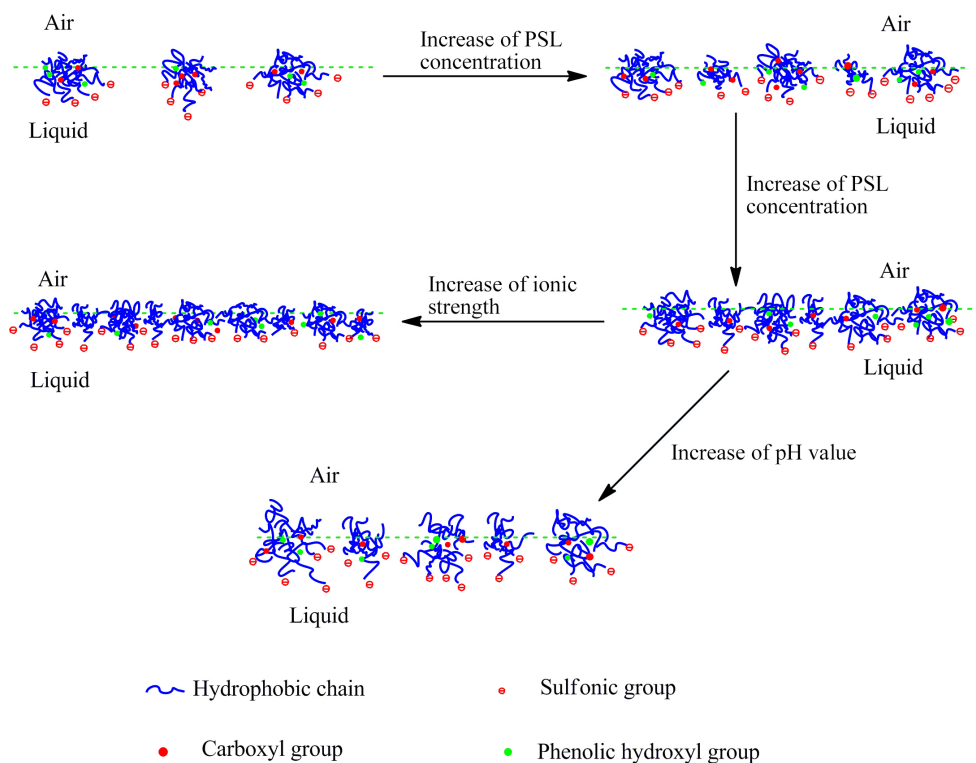
**Figure 7.** The  $A/A_0$  ratio of PSL film at different concentrations of PSL.



**Figure 8.** The  $A/A_0$  ratio of PSL film at different pH values, the concentration of PSL is  $0.5 \text{ g L}^{-1}$ .



**Figure 9.** The  $A/A_0$  ratio of PSL film at different ionic strengths, the concentration of PSL is  $0.5 \text{ g L}^{-1}$ .



**Figure 10.** The adsorption configuration of PSL molecules at the air/liquid interface.

According to our previous analysis in the present work, the adsorption amount of PSL molecules at air/liquid interface *per* film area is higher at higher concentration of PSL, lower pH values and higher ionic strength. Thus, we can conclude that the more the PSL molecules adsorb at air/liquid interface *per* area unit, the worse the stability of the film.

#### The adsorption mechanism at the air/liquid interface

PSL molecule in solution can be approximated to a spherical configuration, the core of a PSL molecule is formed by hydrophobic chain. Sulfonic groups as well as a few phenolic hydroxyl groups mainly cover the surface of PSL molecule, and the carboxyl groups are mainly located in the core of PSL molecule.<sup>11</sup> The surface area of PSL molecule with few of sulfonic groups easily adsorbs at the air/liquid interface because of its stronger hydrophobicity. In addition, the size of PSL molecule in solution is not uniform with a wide molecular weight distribution; PSL molecules with larger molecular weight will preferentially adsorb at the air/liquid interface because of its higher hydrophobicity.<sup>17</sup> Then PSL molecules with smaller molecular weight will adsorb at the air/liquid interface when the concentration of PSL increases. The arrangement configuration of PSL molecules will change from disorder to regularly and tightly when the adsorption

amount of PSL molecules at the air/liquid interface reaches a certain degree; the diagram of adsorption process is shown in Figure 10.

There are some weakly ionized groups such as carboxyl and phenolic hydroxyl at the air/liquid interface because the hydrophobicity core of PSL molecule contains these groups. The weak groups will ionize as the pH value increases, so the PSL molecules will arrange from tightly to loose due to the electrostatic repulsion. While the ionic strength increases, the PSL molecules will array from loose to tightly as a result of electrostatic shielding.

#### Conclusions

The adsorption mechanism of PSL molecules at the air/liquid interface was revealed by studying the influence of concentration of PSL, pH value and ionic strength of PSL solution on the dynamic surface tension and the property of the air/liquid interface film. The adsorption configuration of PSL molecules at the air/liquid interface is related to the content of sulfonic and the ionization degree of weakly ionized groups in PSL molecule; the more the content of sulfonic and the greater the ionization degree in PSL molecule, the looser the PSL molecules arrange at the air/liquid interface and the less ability of PSL to reduce the surface tension of water. The adsorption configuration of PSL molecules at the air/liquid interface can be adjusted by

chemical modification to control the content of hydrophilic groups in PSL molecule and changing the pH value or ionic strength of solution.

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