A Novel Cationic Lignin-amine Emulsifier with High Performance Reinforced *via* Phenolation and Mannich Reactions

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A novel cationic lignin-amine emulsifier with high surface activity was prepared from kraft lignin (KL) *via* the phenolation of KL to obtain phenolated kraft lignin (PKL) and improve reaction sites. The introduction of dehydroabietyl groups as hydrophobic groups and diethylenetriamino groups as hydrophilic groups in PKL, by Mannich reactions, enhanced the performance of the emulsifier. The results showed that the number of the hydroxyphenyl groups in PKL was $0.27/C_9$ unit when 1 mol lignin was treated with 10 mol phenol at 60 °C for 6 h under 60 wt% sulfuric acid. The numbers of dehydroabietyl groups and diethylenetriamino groups in PKL were $0.18/C_9$ and $0.13/C_9$ unit, respectively. The surface tension of the emulsifier was 30.03 mN·m^{-1} at a concentration of 0.03 M hydrochloric acid aqueous solution with a pH 2.0, which is close to the commercial surfactant cetyltrimethylammonium bromide (CTAB). The zeta potential of the emulsifier was 45.1 mV, and its emulsifiability was 72 min. In contrast, the surface tension of the emulsifier prepared by non-phenolated lignin at the same condition was 38.67 mN·m^{-1}, where the maximum zeta potential was 40.03 mV and its emulsifiability was 53 min. As expected, the performance of the emulsifier was reinforced by the phenolation reaction.

Keywords: Lignin-amine; Emulsifier; Phenolation reaction; Mannich reaction

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INTRODUCTION

Lignin is the second most abundant naturally occurring aromatic polymer, existing widely in various kinds of seed plants. Unfortunately, only 1 to 2% of technical lignin (mainly lignosulfonate) isolated from spent pulping liquors has been utilized in industry (Lora and Glasser 2002; Luong *et al.* 2012). Most lignin is burned as fuel or disposed of as waste (Clark 2007; Suhas *et al.* 2007; Nyrud *et al.* 2008; Ibrahim *et al.* 2012), which results in increased greenhouse gases and also the loss of a valuable biomass resource. Therefore, it is worthwhile to develop high value-added chemicals or functional materials from lignin, which has potential as a raw material for the production of these materials (Gundersen *et al.* 2001; Kovalcik *et al.* 2015). The conversion of technical lignin to surfactant is an important utilization of this renewable resource as a functional material (Vishtal and Kraslawski 2011; Duval and Lawoko 2014).

Technical lignin and its derivatives as surfactants have been studied extensively for decades, and there are numerous applications in industrial areas (Gosselink *et al.* 2004; Guigo *et al.* 2010; Chen *et al.* 2014; Zhou *et al.* 2014). Lignosulfonate is widely used as an anionic surfactant on account of its amphipathic structure in dye dispersants (Milczarek

2010), oil displacement agents (Laurichesse and Avérous 2013), water reducers for concrete (Yang *et al.* 2008), additives for coal-water slurry (Nadif *et al.* 2002), drilling-fluid additives, *etc*. (Homma *et al.* 2008). Kraft lignin (KL) can be used as an anionic surfactant after being sulfonated, a cationic surfactant for asphalt emulsification (Rachor and Ludwig 1975; Matsushita *et al.* 2003), in wastewater treatment after modification as lignin-amine, or as a quaternary ammonium salt (Fang *et al.* 2010). However, the surfactants derived from lignin usually have low surface activity and are only used as low value-added products because they contain no typical hydrophobic groups. Therefore, it is necessary to add hydrophobic groups in lignin to enhance its surface activity. Moreover, the introduction of cationic hydrophilic groups in lignin is essential if a lignin derivative is to be used as a cationic surfactant (Košíková *et al.* 2000; Shulga *et al.* 2002).

Previously, KL was converted into cationic asphalt emulsifiers by the introduction of hydrophilic and hydrophobic groups (Liu *et al.* 2013). However, functional groups could only be added to reactive sites in KL. It is important to increase reactive sites to introduce more amphipathic groups in lignin and further improve its performance.

There are several effective ways to enhance the reactivity of lignin (Alonso *et al.* 2005; Hu *et al.* 2011), especially for sulfuric acid lignin. One pathway is to react lignin with sulphide, which can remove methoxy groups, thus increasing its reactive sites (Wu and Zhan 2001; Hu *et al.* 2014). Phenolation, *i.e.*, treating lignin with phenol, (Effendi *et al.* 2008), is also a low-cost, effective approach for enhancing lignin reactivity.

The emulsifiers prepared by lignin-amine bearing diethylenetriamino groups usually have strong positive charges at pH 2, and thus have better stability (Liu *et al.* 2013). Rosin and its derivatives show good surface activity (Jia *et al.* 2009; Atta *et al.* 2009, 2011, 2013). Therefore, if rosin or its derivatives are introduced in phenolated lignin as hydrophobic groups, and diethylenetriamino groups as hydrophilic groups, the properties of the lignin-amine emulsifier are expected to improve. Herein, a novel lignin-amine cationic emulsifier prepared from KL is presented, in which KL was phenolated to improve reaction sites. Subsequently, dehydroabietyl groups and diethylenetriamino groups were introduced to PKL *via* Mannich reactions. The surface tension, zeta potential, emulsifiability, and foamability of this emulsifier were evaluated. This emulsifier was determined to be suitable for use as a cationic asphalt emulsifier in road construction and road maintenance.

EXPERIMENTAL

Materials

Kraft lignin was recovered as a water-insoluble precipitate from the spent liquor of the sulfate pulping of pine wood, provided by Guangxi Nanning Phoenix Pulp & Paper Co. Ltd, Nanning, China. N-(2-aminoethyl)dehydroabietamide was prepared from dehydroabietic acid as has been described (Liu *et al.* 2013). Other chemicals and solvents were commercially available as standard laboratory-grade reagents and used without further purification.

Methods

Preparation of phenolated kraft lignin (designated as PKL)

A mixture of 10.00 g of KL, 63.00 g of phenol, and 150 mL of 60 wt% sulfuric acid was added to a 500-mL round-bottomed flask equipped with a condenser and a stir bar. The

mixture was heated to 60 °C with stirring in an oil bath for 6 h. After quenching by dilution with 5600 mL of water, the suspension was boiled for 3 h. The solid was separated by filtration, washed several times with warm water (90 °C) to thoroughly remove free phenol, dried in a vacuum oven at 50 °C overnight, and characterized by Fourier transform infrared spectroscopy (FT-IR; described below) (Matsushita and Yasuda 2003). The content of phenolic hydroxyl groups was determined by Folin-Ciocalteu methods.

Preparation of N-(2-aminoethyl)dehydroabietamide/formalin-modified KL (or PKL) (designated as ADRA-F-KL or ADRA-F-PKL, respectively)

First, 2.00 g of KL (or PKL) and 20 mL of pyridine were added to a 100-mL round-bottomed flask equipped with a condenser, stir bar, and thermometer. The mixture was heated to 90 °C, and a mixture of 0.855 g of N-(2-aminoethyl)dehydroabietamide dissolved in 20 mL of pyridine and 0.19 mL of 37 wt% formalin (F) was then charged dropwise to the flask. After being stirred for another 3 h, pyridine was recovered by evaporation under vacuum. Then, 30 mL of 10.0 wt% sodium hydroxide aqueous solution was added to the flask to dissolve the resulting solid until the pH of the solution was adjusted to 11.0. The insoluble adduct in the solution, which was formed by the reaction of N-(2-aminoethyl)dehydroabietamide with formalin, was removed by filtration. After three extractions with 10 mL of toluene, the filtrate was acidified with 1.0 M hydrochloric acid to pH 2.5 to precipitate modified KL (or PKL). The solid was separated by filtration, washed with water until the pH was approximately 7.0, and then dried in a vacuum oven at 50 °C overnight to obtain ADRA-F-KL (or ADRA-F-PKL). The samples were characterized by FT-IR, and the content of dehydroabietyl groups was determined by Folin-Ciocalteu methods.

Preparation of diethylenetriamine/formalin-modified ADRA-F-KL (or ADRA-F-PKL) (designated as DETA-ADRA-F-KL or DETA-ADRA-F-PKL, respectively)

A mixture of 2.00 g ADRA-F-KL (or ADRA-F-PKL), 50 mL of water, and a 10 mL of 10.0 wt% sodium hydroxide solution was added to a 100-mL round-bottomed flask equipped with a condenser, a stirrer bar, and a thermometer. The mixture was gently heated and stirred until the ADRA-F-KL (or ADRA-F-PKL) dissolved completely, and the pH of the solution was 11.0. The mixture was then heated to 90 °C, and a mixture of 2.06 g diethylenetriamine and 1.52 mL of 37 wt% formalin (F) was then charged dropwise to the flask. After being stirred for another 3 h, the solution was acidified with 1.0 M hydrochloric acid to a pH between 5.5 and 6.0 to precipitate the modified product DETA-ADRA-F-KL (or DETA-ADRA-F-PKL).

The suspension was purified by dialysis in water for several days until no chloride ion was detected in the dialyzate. The solid was obtained by filtration, washed with cooled water, dried in the vacuum oven at 50 °C overnight, and characterized by FT-IR. The content of diethylenetriamino groups was determined by Folin-Ciocalteu methods. The synthesis route for DETA-ADRA-F-PKL is shown in Fig. 1.

Preparation of diethylenetriamine/formalin-modified KL (or PKL) (designated as DETA-F-KL or DETA-F-PKL, respectively)

DETA-F-KL (or DETA-F-PKL) was prepared according to the same procedure, changing DETA-F-KL (or DETA-F-PKL) to KL (or PKL).
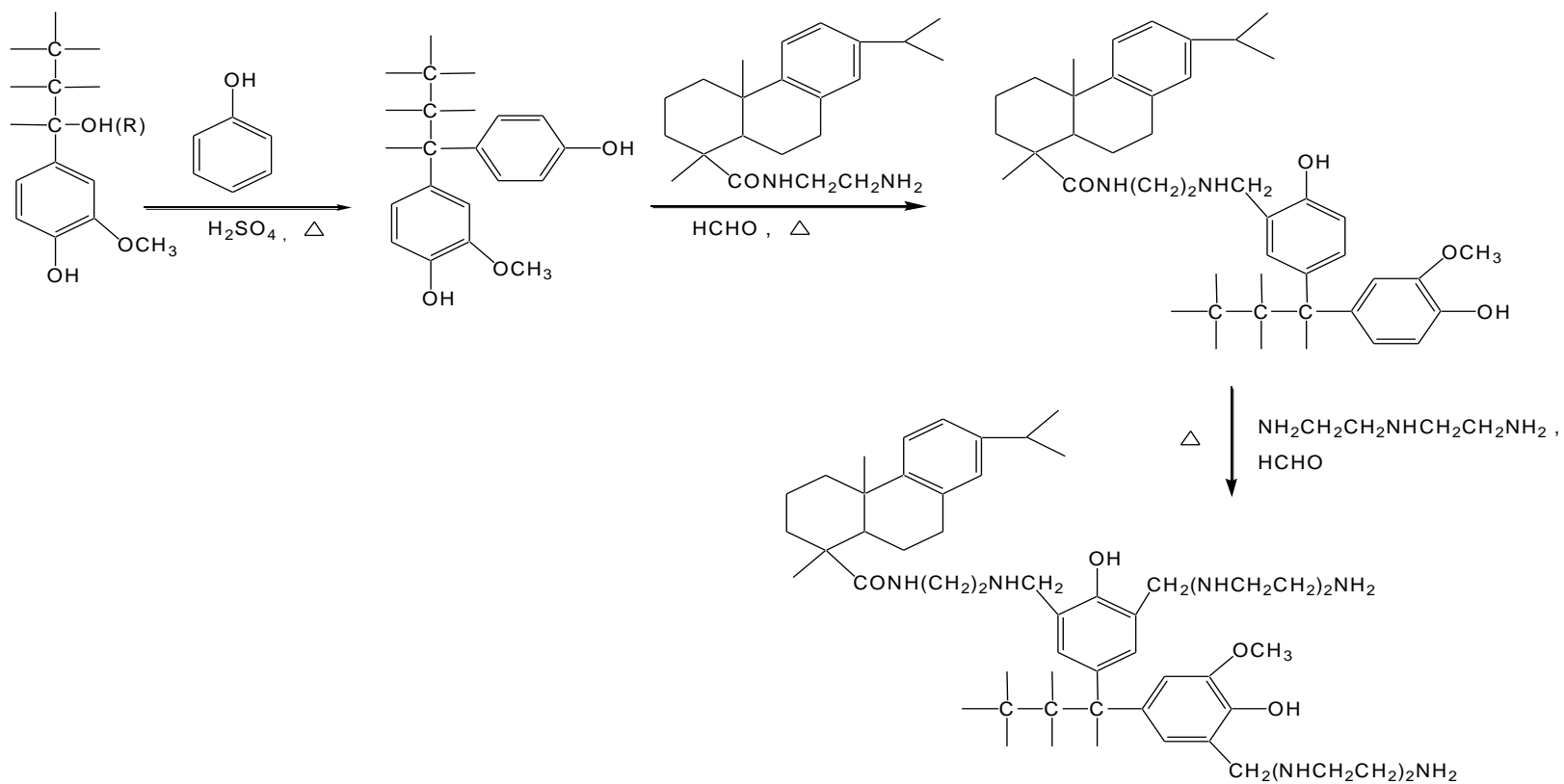
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Fig. 1. Synthesis of DETA-ADRA-F-PKL

Characterization techniques

The phenolic hydroxyl groups in the samples were measured with the Folin-Ciocalteu reagent using an Agilent Cary 60 ultraviolet-visible spectrophotometer (Agilent, Santa Clara, CA, USA) at 760 nm. Phenol was used as a standard. The exact concentration of phenol standard solution was titrated by potassium bromate-iodometry. Working standards of phenol were prepared from a diluted phenol standard solution (Sousa *et al.* 2001) (see supplement).

The molecular weights were measured with a Shimadzu LC-20AT gel permeation chromatograph (Kyoto, Japan) equipped with an RID-10A refractive-index detector connected with three Waters Styragel gel columns (HR1, HR3, and HR4; Milford, USA) and a guard column with a mobile phase of THF at 30 °C, a flow rate of 1.00 mL·min^{-1}, and polystyrene as a standard.

The FT-IR spectra of the samples were obtained on a Nicolet FT-IR Impact 410 spectrophotometer (Nicolet, Madison Wisconsin, USA) equipped with OMNIC analyzing software in the wavenumber range from 4,000 to 500 cm^{-1} by the conventional potassium bromide pellet method.

The zeta potential was measured at room temperature using a Zetasizer (Nano-ZS, Malvern Instruments, Melvin, UK), which worked on the principle of dynamic light scattering. The samples were dissolved in a dilute hydrochloric acid aqueous solution, and the pH was adjusted to 2.00. The solution was then diluted to different concentrations with 0.0100 M hydrochloric acid. This dilution factor was chosen to ensure that the maximum concentration used for the measurement was ≤ 0.03 M, according to the manufacturer's specification. Measurements were performed in quadruplicate, and the average values were calculated.

Surface tension measurements were carried out with the ring method using a JK99A Tensiometer (Heng Ping Instruments, Shanghai, China). Deionized water (electrical resistivity = 18.2 MΩ·m^{-1}) was used in this measurement. The samples were prepared following the above-mentioned procedure in the zeta potential measurements and then diluted to different concentrations with 0.0100 M hydrochloric acid. Thirty minutes after the solution was added to a measurement dish, the surface tension was measured. Measurements were performed in quadruplicate, and the average values were calculated.

Measurements of the foamability and emulsifiability were performed with 1.0000 g of sample, which was heated to dissolution in dilute hydrochloric acid, adjusted to a pH of 2.00, and diluted to 200.00 mL with 0.0100 M hydrochloric acid. Then, 30.00 mL of the sample solution and 20.00 mL of toluene were added to a 100-mL graduated cylinder with a stopper.

The stopper was covered, and the cylinder was shaken from top to bottom violently for six times, then left to stand for 1 min; this procedure was performed six times, until the toluene and water became a homogeneous mixture. The foamability was obtained by counting the foam volume when the toluene was mixed completely with the sample solution, both immediately afterwards and after leaving the foam to stand for 5 min.

The water separation time was recorded immediately when the volume of water was exactly 20.00 mL. The separation time was used to evaluate the relative emulsifiability of samples.

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RESULTS AND DISCUSSION

Conditions of KL Phenolation

The phenolation reaction of KL was studied by varying phenol dosage, reaction temperature, and the concentration of sulfuric acid (Table 1). The reaction condition had a noticeable influence on the content of the phenol hydroxyl groups in PKL. For the molar ratio of phenol to KL (provided the amount of substance was calculated by C_9 units in KL, and the molecular weight of C_9 units of KL was 180) (Robert *et al.* 1984) ranging from 0:1 to 10:1, the phenolic hydroxyl groups in PKL increased from 3.05 mmol·g^{-1} to 3.97 mmol·g^{-1}. This result indicated that the hydroxyphenyl groups introduced by phenolation numbered 0.26 for each C_9 unit of KL. However, when the phenol dosage was increased to 20:1, the content of phenolic hydroxyl groups was 3.79 mmol·g^{-1}, indicating that phenol reached saturation when it was over 10:1 (Entries 1, 2, 3, 4, and 5). With the increasing reaction temperature from 40 °C to 60 °C, the phenolic hydroxyl groups increased from 3.37 mmol·g^{-1} to 3.97 mmol·g^{-1}, but when reaction temperature was increased progressively to 70 °C, the phenolic hydroxyl groups had a slight decrease instead (Entries 6, 7, 8, and 9). An increase in phenolic hydroxyl groups was also observed with the increase of the concentration of sulfuric acid from 40 to 60 wt% (Entries 10, 11, and 8).

Notably, the phenol hydroxyl groups slightly declined when the concentration of sulfuric acid was up to 72 wt% (Entry 4). This was because there may be two competitive reactions in the reaction system. One was the phenolation reaction, which would increase phenolic hydroxyl groups; the other was the condensation reaction between the molecules in KL under thick sulfuric acid catalysis, which would decrease phenolic hydroxyl groups. The condensation would become increasingly stronger when the reaction temperature was too high, and (or) the concentration of sulfuric acid was very thick.

Table 1. The Influence of Reaction Conditions on the Lignin Phenolation

Entries	n_{Phenol}:n_{Lignin}	Con. of sulfuric acid （wt %）	Time (h)	Temp. (°C)	Phenolic hydroxyl groups (mmol·g^{-1})	M_w	M_n	M_w/M_n
1	0:1	72	6	60	3.05	5134	1796	2.86
2	1:1	72	6	60	3.22	5106	2420	2.11
3	5:1	72	6	60	3.59	5080	2442	2.08
4	10:1	72	6	60	3.85	5056	2767	1.83
5	20:1	72	6	60	3.79	5032	2710	1.86
6	10:1	60	6	40	3.37	5409	2740	1.97
7	10:1	60	6	50	3.62	5320	2720	1.96
8	10:1	60	6	60	3.97	5201	2617	1.99
9	10:1	60	6	70	3.82	5042	2667	1.89
10	10:1	40	6	60	3.45	5268	2315	2.28
11	10:1	50	6	60	3.69	5257	2681	1.96

Analysis of the gel permeation chromatograph (GPC) obtained for the PKL showed that the weight-average molecular weight was slightly increased from 5134 to 5201, and M_w/M_n changed from 2.86 to 1.99 (Entry 8). This data indicated that, in terms of the molecular weight of the PKL, the phenolation reaction almost had no effect on PKL that would be modified as an emulsifier in the subsequent reaction.

Overall, the optimum conditions of phenolation reaction were as follows: molar

ratio of phenol to lignin, 10:1; sulfuric acid concentration, 60 wt%; reaction temperature, 60 °C; and reaction time, 6 h.

Preparation of the Lignin-Amine Emulsifiers

As technical lignin has an amphiphilic structure, it can be used as a cationic emulsifier after introducing diethylenetriamino groups as cationic hydrophilic groups. Because its surface activity is low, it can just be used as a co-emulsifier. To improve its surface activity, hydrophobic groups like high fatty amine, rosin, or its derivatives, are usually introduced in KL. The phenolation of KL was first adopted to improve reactive sites, and then diethylenetriamino groups and dehydroabietyl groups were introduced consecutively in PKL to obtain excellent cationic emulsifiers with high surface activity. The amount of hydroxyphenyl groups introduced by phenolation for each C_9 unit of KL (X) was calculated from phenolic hydroxyl data using Eq. 1.

$$X = (C_1-C_0) \times 180 / (1000 -93.11 \, C_1) \tag{1}$$

The amounts of diethylenetriamino groups and dehydroabietyl groups in KL or PKL are shown in Table 2. The numbers of per C_9 unit (X_1) was calculated from phenolic hydroxyl data using Eq. 2,

$$X_1 = (C_0-C_1) \times M_1 / (M_2 \times C_1) \tag{2}$$

where C_0 and C_1 are the phenolic hydroxyl content of substrate or product (mmol·g^{-1}), respectively; 180 is the formula weight of C_9 unit in KL; 93.11 is the formula weight of hydroxyphenyl group; M_1 is the formula weight of C_9 unit in substrate; and M_2 is the formula weight of the groups introduced, 355 for the dehydroabietyl group, 116 for the diethylenetriamino group, respectively. The formula weight (M) was calculated from the number of groups per C_9 unit using Eq. 3,

$$M = 179 + X \, (\text{or } X_1) \times M_2 \tag{3}$$

where 179 is the formula weight of the KL C_9 group. In sum, 0.18/C_9 unit of (the numbers of per C_9 unit) dehydroabietyl groups toward ADRA-F-PKL were introduced in PKL *via* Mannich reactions among PKL, N-(2-aminoethyl)dehydroabietamide, and formalin (Entry 2). In contrast, only 0.045/C_9 unit of dehydroabietyl groups toward ADRA-F-KL were introduced in KL (Entry 3). Similarly, there were 0.13/C_9 unit of diethylenetriamino groups in DETA-ADRA-F-PKL introduced *via* Mannich reactions among ADRA-F-PKL, diethylenetriamine, and formalin (Entry 4), and only 0.09/C_9 unit of diethylenetriamino groups in DETA-ADRA-F-KL (Entry 5).

Table 2. Diethylenetriamino and Dehydroabietyl Groups in KL or PKL

Entry	Sample	Phenolic Hydroxyl (mmol·g^{-1})	Groups Introduced (per C_9 unit)	Formula Weight
1	KL	3.05	-	180
2	ADRA-F-PKL	3.04	0.18	267
3	ADRA-F-KL	2.80	0.045	195
4	DETA-ADRA-F-PKL	2.88	0.13	282
5	DETA-ADRA-F-KL	2.66	0.09	205
6	PKL	3.97	0.26	203
7	DETA-F-PKL	3.33	0.34	242
8	DETA-F-KL	2.83	0.12	193

These results indicated that once KL was phenolated to PKL, the numbers of dehydroabietyl groups and diethylenetriamino groups increased by 3-fold and 0.44-fold, respectively. A similar situation was found in Entries 7 and 8. The numbers of diethylenetriamino groups in DETA-F-PKL was $0.34/C_9$ unit (Entry 7). In contrast, there was only $0.12/C_9$ unit of diethylenetriamino groups in DETA-F-KL (Entry 8). The numbers of diethylenetriamino groups increased by 1.83 when KL was phenolated to PKL, which was attributed to the increase of reactive sites in PKL.

FT-IR Characterization of the Lignin-Amine Emulsifiers

The FT-IR spectra of KL and its derivatives (Fig. 2) showed that the peak at 1032 cm^{-1}, assigned to C-O stretching vibration of aromatic guaiacol primary alcohol and ether bond in PKL, became weaker compared with KL. This result reflected that C-O bonds at the C_α sites in KL were replaced by C-C bonds derived from the reaction of KL with phenol in the o- and/or p-position. Furthermore, a new band at 755 cm^{-1}, which was assigned to the C-H plane deformation vibration in o- or p-hydroxylphengl groups, appeared in PKL (Matsushita and Yasuda 2005).
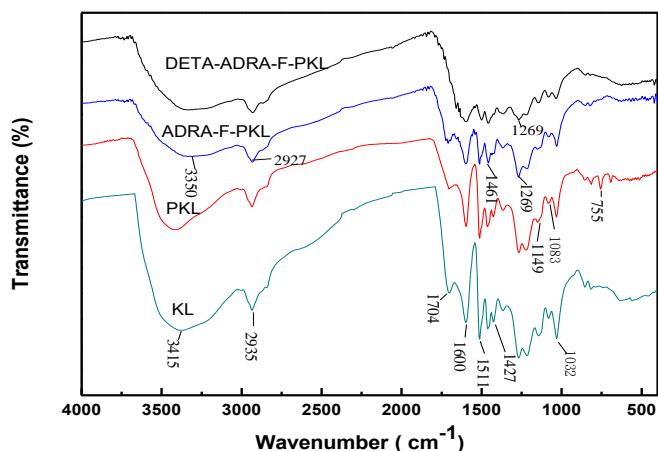

Fig. 2. FT-IR spectra of KL, PKL, ADRA-F-PKL, and DETA-ADRA-F-PKL

The FT-IR spectrum of ADRA-F-PKL showed that, in comparison with PKL, the band at 3350 cm^{-1}, which was assigned to O-H and N-H stretching vibrations, became broader and stronger, and reached a redshift of 65 wave numbers. The peaks at 2934 cm^{-1} and 1461 cm^{-1}, assigned to C-H stretching vibration and bending vibration, respectively, became more pronounced with respect to the peak at 1511 cm^{-1}. This data showed that ADRA-F-PKL was obtained. When ADRA-F-PKL was further reacted with DETA and formalin, the peaks at 3350 cm^{-1}, 2927 cm^{-1}, and 1461 cm^{-1} in DETA-ADRA-F-PKL became more pronounced. However, the peak at 1269 cm^{-1}, assigned to O-CH_3 stretching vibration, became weaker. This effect may be attributed to the decreased relative content of methoxyl groups in DETA-ADRA-F-PKL.

Evaluation of the Lignin-Amine Emulsifiers

The performance of the lignin-amine emulsifiers was evaluated in terms of its zeta potential, surface tension, foamability, and emulsifiability. All measurements were performed in an aqueous solution at pH 2.00.
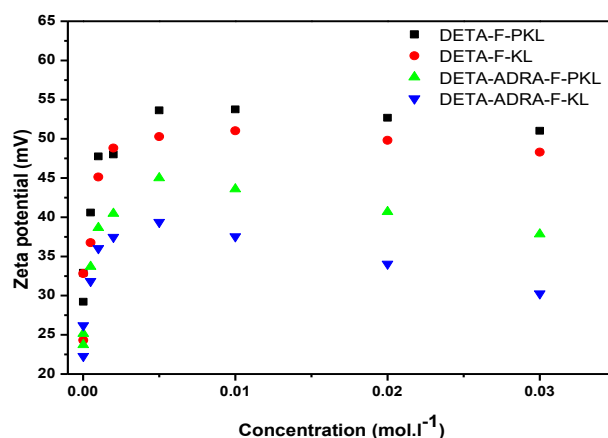
Fig. 3. Relationship between the zeta potentials and the concentration of lignin-amine emulsifiers in an aqueous solution at pH 2.00

Zeta Potential of the Lignin-Amine Emulsifiers

The zeta potential of DETA-F-KL, DETA-F-PKL, DETA-ADRA-F-KL, and DETA-ADRA-F-PKL were explored at room temperature by varying the concentration of the samples (Fig. 3). The zeta potentials of the four lignin-amine emulsifiers showed a similar tendency, which increased to the maximum at first, and then decreased slightly with further increasing of the concentration. This may be caused by the fact that the aggregates of lignin-amine emulsifiers in aqueous solutions became bigger until the attraction and repulsive forces between the colloidal particles were balanced, leading to the rapid increase in the zeta potential of the colloidal particles. As the concentration increased further, the zeta potential decreased slightly because of the compression of the electric double layer by counterions. Figure 3 also shows that the emulsifiers derived from PKL (DETA-F-PKL or DETA-ADRA-F-PKL) had higher zeta potentials than corresponding emulsifiers derived from KL (DETA-F-KL or DETA-ADRA-F-KL) under the same conditions. This result reflected that PKL had more reactive sites and introduced more diethylenetriamino groups. Thus, the emulsifiers derived from PKL presented stronger positive charges compared with those derived from KL. According to the DLVO theory, the higher the absolute value of the charge is, the greater the mutual repulsion between the micelles is. Therefore, the emulsion produced by the phenol-modified emulsifiers had better stability.

Surface Tension of the Lignin-Amine Emulsifiers

The surface tension of four lignin-amine emulsifiers and cetyltrimethylammonium bromide (CTAB) is shown in Fig. 4. With increasing concentration, the surface tension of lignin-amine emulsifiers decreased gradually, but they did not reach critical micelle concentration (CMC) until at the concentration of 0.03 M. However, CTAB reached CMC at very low concentration. The difference was possibly because the emulsifiers derived from KL were polymers with three-dimensional networks and could not orientate and pack closely like CTAB molecules at the water-air interface. The surface tension of the emulsifiers derived from PKL was lower than that of the corresponding emulsifiers derived from KL because the former had higher zeta potential than the latter. As the same charges repelled one another, this made the chains of the emulsifier molecules derived from PKL more extended. Thus, this effect was favorable to the orientation and packing in the

interface for the emulsifier molecules, so they showed a lower surface tension. Figure 4 also indicates that the surface activity was improved by the introduction of hydrophobic dehydroabietyl groups due to more regular and compact packing on the water-air interface. When the concentration was 0.03 M, the surface tension of DETA-ADRA-F-PKL reached 30.03 mN·m⁻¹, which approached that of the commercial surfactant CTAB (23.12 mN·m⁻¹ at CMC).
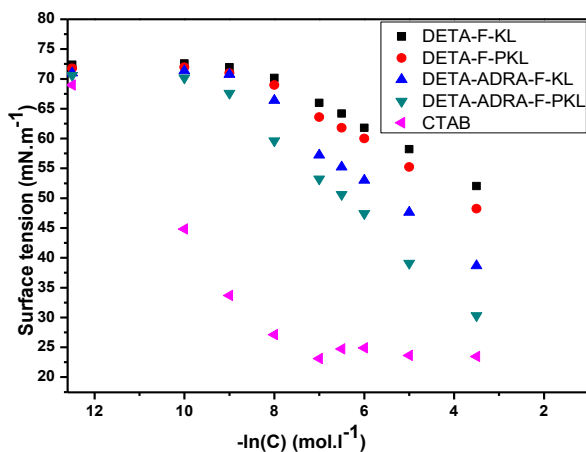

Fig. 4. Variation of surface tension with the concentration of lignin-amine emulsifiers at pH 2.00 and CTAB in an aqueous solution

Based on the relationship between the surface tension and the concentration of the emulsifiers, the surface excess concentration (Γ) and the area per molecule (A) of the lignin-amine emulsifiers at the interface were calculated (Table 3). The surface excess concentration was calculated from surface tension data using Eq. 4,

$$\Gamma = 1 / nRT \times (-d\gamma / d\ln C) \tag{4}$$

where ($-d\gamma / d\ln C$) is the slope of the plot of γ *versus* $\ln C$ at constant temperature (T), n is a constant, which depends on the type and degree of ionization of the emulsifiers, R is the gas constant (8.314 J·mol⁻¹·K⁻¹), γ is the surface tension, and C is the concentration of emulsifiers. The Γ values were used for calculating the area per molecule at the interface using Eq. 5,

$$A = 10^{14} / N_A\Gamma \tag{5}$$

where N_A is Avogadro's constant (6.02 × 10²³ mol⁻¹). The A value provides information on the degree of packing and the orientation of the adsorbed emulsifiers at the interface. As shown in Table 3, under the same concentration, the DETA-ADRA-F-PKL had the smallest molecular sectional area among the four lignin-amine emulsifiers. There were two major reasons for this experimental phenomenon. First, phenolation reinforced the positive charges of the emulsifiers and made the emulsifier macromolecules chains spread well, promoting the orientation at the water-air interface. Secondly, the introduction of hydrophobic groups in DETA-ADRA-F-PKL allowed the emulsifier molecules to pack closely at the interface. However, the DETA-ADRA-F-PKL molecule had larger dimensions than CTAB because DETA-ADRA-F-PKL was a polymer emulsifier with a sphere-like structure, and its chains could not orientate as well as CTAB molecules.

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Table 3. The Surface Excess Concentration and the Area Per Molecule of Lignin-Amine Emulsifiers and CTAB

Sample	-dγ/dln C	C_{max} (mol·l^{-1})	γ (mN·m^{-1})	Γ (10^{-10} mol·cm^{-2})	A (nm^2)
DETA-F-KL	3.73	0.03	52.04	0.75	2.21
DETA-F-PKL	4.24	0.03	48.23	0.86	1.93
DETA-ADRA-F-KL	5.86	0.03	38.67	1.18	1.41
DETA-ADRA-F-PKL	6.76	0.03	30.03	1.36	1.22
CTAB	8.62	C_{cmc}=9×10^{-4}	23.12	1.76	0.94

Foamability and Emulsifiability of the Lignin-Amine Emulsifiers

The foamability of lignin-amine emulsifiers was measured by counting the foam volume when toluene was mixed with a sample solution. Measurements were taken both immediately after mixing and after leaving the foam to stand for 5 min. The separation time of water from toulene was recorded immediately when the volume of water was exactly 20 mL. The separation time was used to evaluate the relative emulsifiability of samples.

The data in Table 4 indicate that the groups of DETA-ADRA-F-KL and DETA-ADRA-F-PKL had stronger foamability than the groups of DETA-F-KL and DETA-F-PKL, and the foamability of DETA-ADRA-F-PKL was stronger than that of DETA-ADRA-F-KL. This is because the surface tension of the former was lower than that of the latter. It should be noted that the emulsifiability of emulsifiers derived from PKL was better than that of the corresponding emulsifiers derived from KL. The ADRA-DETA-F-PKL had the best emulsion stability among the four lignin-amine emulsifiers, which had 72 min of water-oil separating time. In contrast, DETA-ADRA-F-KL only had 53 min. This conclusion was consistent with the zeta potential and surface tension data.

Table 4. Determination of the Foamability and Emulsifiability

Sample	Separation Time (min)	Initial Foam Volume (mL)	Foam Volume After Standing for 5 min (mL)
DETA-F-KL	43	7.5	6
DETA-F-PKL	46	8.5	7
DETA-ADRA-F-KL	53	11	9
DETA-ADRA-F-PKL	72	12	9

CONCLUSIONS

1. DETA-ADRA-F-PKL is a novel lignin-amine emulsifier that was derived from KL *via* phenolation to improve reaction sites. The dehydroabietyl groups and diethylenetriamino groups were introduced to PKL *via* Mannich reactions.

2. The emulsifier exhibited excellent surface activity, high zeta potential, and good emulsifiability for toluene emulsifying.

3. The PKL had more reactive sites, and thus could introduce more hydrophobic groups and hydrophilic groups than KL, which conferred higher zeta potential and surface

activity to the emulsifier. These properties resulted in stronger repellent behaviour between emulsion particles and closer packing of the emulsifier molecules at the oil-water interface.

4. High zeta potential might make the chains of the emulsifier molecules derived from PKL more extended in an aqueous solution, which was conducive to the orientation and closer packing at the water-air interface and, thus, resulted in a lower surface tension.

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