Preparation and Evaluation of a Novel Cationic Amphiphilic Lignin Derivative with High Surface Activity

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A novel cationic amphiphilic lignin derivative with high surface activity was prepared from kraft lignin *via* the introduction of dehydroabietyl groups as lipophilic groups and diethylenetriamine groups as hydrophilic groups by the Mannich and ketone-amine condensation reactions. Solubility, surface tension, hydrophilic-lipophilic balance (HLB) values, foamability, and zeta potential were used to evaluate the basic physico-chemical properties of the cationic amphiphilic lignin derivative. The experiments show that the solubility of the cationic amphiphilic lignin derivative is 2.10 wt%, the critical micelle concentration is 5.0 $g \cdot L^{-1}$, the surface tension is 29.85 $mN \cdot m^{-1}$ at a concentration of 5.0 $g \cdot L^{-1}$, the HLB value is 12, and the foam volume is 11.1 mL initially and 8.0 mL after standing for 5 min in an aqueous solution at pH 2.0.

Keywords: Kraft lignin; Dehydroabietic acid; Diethylenetriamine; Cationic surfactant; Surface activity

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INTRODUCTION

With the depletion and price rise of crude oil, the possibility of using renewable biomass resources to replace fossil resources has been drawing significant worldwide attention during the last decades. Moreover, the use of fossil resources emits abundant greenhouse gases such as carbon dioxide, which leads to global warming (Anders *et al*. 2008). Lignin is the second most abundant renewable organic compound on the earth (Clark 2007; Hu *et al*. 2011), and the most naturally occurring aromatic polymer (Lora and Glasser 2002). To date, only a small percentage of technical lignin (*ca*. 1 to 2%, mainly lignosulfonate) isolated from spent pulping liquors has been utilized in the industry (Lora and Glasser 2002), and most of the lignin is only used as fuel, which is merely a kind of low value-added use, to obtain energy and recover bases in the pulping industry, or be disposed of as waste (Suhas *et al*. 2007; Luo *et al*. 2009). However, it has been reported that lignin has potential as a raw material for the production of chemicals and functional materials (Mohamad Ibrahim *et al*. 2012; Vishtal and Kraslawski 2011; Guigo *et al*. 2010; Gosselink *et al*. 2004). It is necessary to develop high value-added, functional novel materials from lignin to make good use of this kind of renewable resource and promote sustainable development of pulping and papermaking.

Lignin has been converted into surfactants used as emulsifiers (Košíková *et al*. 2000; Homma *et al*. 2008; Matsushita and Yasuda 2003), dispersers (Yang *et al*. 2008; Milczarek 2010; Nadif *et al*. 2002; Matsushita and Yasuda 2005), oil displacement agents (DeBons and Whittington 1992; Gundersen *et al*. 2001), or as detergents (Shulga *et al*. 2011). The authors previously have researched and developed the technology of converting kraft lignin (KL), obtained by the sulfate pulping process, to cationic surfactants (Liu and Wang 2004; Liu *et al*. 2005; Liu *et al*. 2006). Lignin emulsifiers modified by diethylenetriamine render asphalt emulsions that exhibit better adhesion of the asphalt to the mineral aggregates and higher ductility of the basic asphalt. However, it can only be used as a good by-emulsifier because of its surface activity. It follows that higher performance might be achieved by chemical modification to increase the surface activity. Rosin is an abundant renewable bioresource, and its derivatives, such as dresinate, show good surface activity (Atta *et al*. 2009; Jia *et al*. 2009; Atta and Elsaeed 2011; Atta *et al*. 2013). Therefore, if rosin or its derivatives are introduced in lignin as lipophilic groups, the surface activity would be improved. Herein, a novel cationic amphiphilic derivative from kraft lignin *via* the Mannich and ketone-amine condensation reactions is presented, in which dehydroabietic acid groups function as lipophilic groups to depress the water surface tension and diethylenetriamine groups function as hydrophilic groups. The main properties of this kraft lignin derivative were evaluated by solubility, surface tension, HLB values, foamability, and zeta potential. This cationic amphiphilic lignin derivative is intended for use as a cationic asphalt emulsifier, and could have a promising future in road construction and road maintenance.

EXPERIMENTAL

Materials

Kraft lignin was recovered as a water-insoluble precipitate from spent liquor of the sulfate pulping of pine wood, provided by Guangxi Nanning Phoenix Pulp & Paper Co. Ltd. High purity dehydroabietic acid (95 wt%, measured by gas chromatography) was isolated from disproportionated rosin provided by Wuzhou Sun Shine Forestry & Chemicals Co. Ltd. Other chemicals and solvents were commercially available as standard laboratory-grade reagents and used without further purification.

Methods

Preparation of dehydroabietyl chloride (DC)

A mixture of 40.0 g of dehydroabietic acid (DA) and 50 mL anhydrous benzene was added to a 250-mL round-bottomed flask equipped with a condenser and a stirrer bar. Then, 24 mL of $SOCl_2$ was added dropwise with continuous stirring at room temperature. The mixture was then slowly heated to 75 to 80 °C and stirred for another 2.5 to 3 h until there was no acidic gas to release (the gas was absorbed by a diluted sodium hydroxide aqueous solution). Once the reaction was complete, benzene and residual $SOCl_2$ were removed by evaporation under vacuum to obtain dehydroabietyl chloride in 95% yield. The samples were measured by FT-IR.

Preparation of N-(2-aminoethyl) dehydroabietamide (DAEA)

A mixture of 0.9 mol of ethylenediamine, 0.5 mL of triethylamine, and 40 mL of anhydrous tetrahydrofuran was added to a 250-mL round-bottomed flask equipped with a condenser and a stirrer bar. Then, 0.3 mol of dehydroabietyl chloride dissolved in 40 mL of anhydrous tetrahydrofuran was added dropwise with stirring in an ice bath, and the mixture was then slowly heated to 80 °C. After 2.5 h of reaction, the salt obtained was removed by filtration, and the solvent and residual ethylenediamine were recovered by evaporation under vacuum. The solid was washed with DI water and purified by preparative high performance liquid chromatography (HPLC) to yield N-(2-aminoethyl) dehydroabietamide. The samples were measured by FT-IR and ^{1}H-NMR.

Preparation of kraft lignin modified by N-(2-aminoethyl) dehydroabietamide/formalin (KL/DAEA/F)

First, 1.80 g of purified lignin and 20 mL of pyridine were added to a 100-mL round-bottomed flask equipped with a condenser, a stirrer bar, and a thermometer. The mixture was heated to 90 °C, and a mixture of 0.025 mol of N-(2-aminoethyl) dehydroabietamide dissolved in 20 mL of pyridine and 2.48 mL of 37 wt % formalin (F) was then charged dropwise to the flask. After being stirred for 2.5 h, pyridine was recovered by evaporation under vacuum at *ca.* 50 °C. Then, a 5 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. The insoluble adducts in the solution, which formed by the reaction of N-(2-aminoethyl) dehydroabietamide with formalin, were removed by filtration. After being extracted with 10 mL of toluene three times, the filtrate was acidified with 1 M hydrochloric acid to pH 2.5 to precipitate modified kraft lignin. The solid was obtained by filtration, washed with DI water until the pH was *ca.* 7, then dried at 50 °C and characterized by elemental analysis and FT-IR. The nitrogen content of the synthesized sample is listed in Table 1.

Preparation of kraft lignin modified by N-(2-aminoethyl) dehydroabietamide/ diethylenetriamine/formalin(KL/DAEA/DETA/F) and kraft lignin modified by diethylenetriamine/formalin (KL/DETA/F)

The synthesis route for KL/DAEA/DETA/F is as shown in Fig. 1.

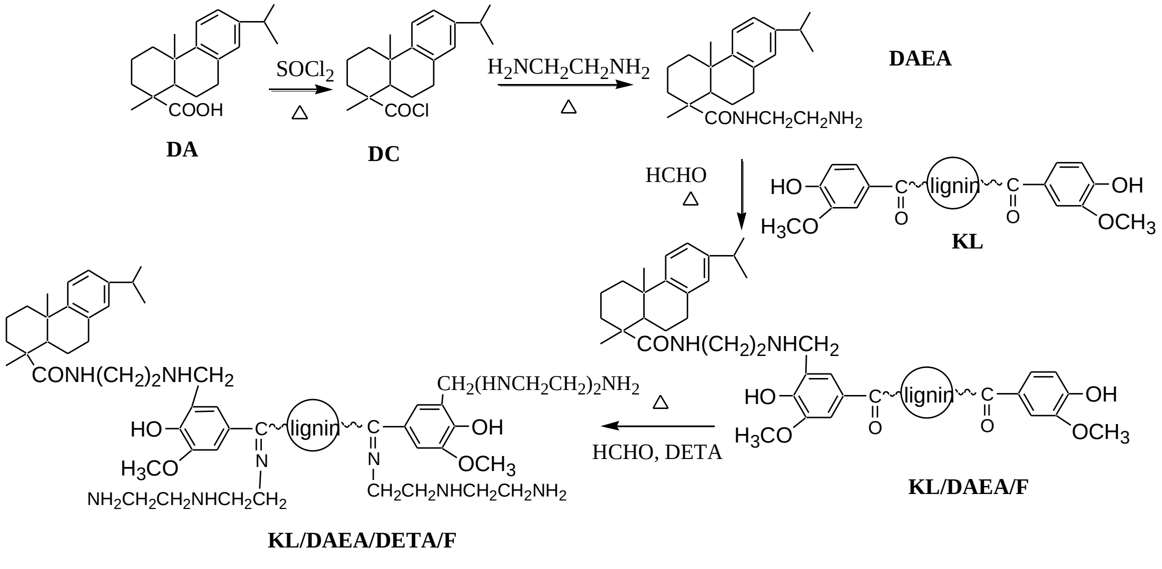

Fig. 1. Synthesis route for KL/DAEA/DETA/F

A mixture of 1.80 g of KL/DAEA/F or KL dissolved in 1 mol·L^{-1} NaOH solution until the pH was *ca.* 9.0, and 0.017 mol of diethylenetriamine was added to a 100-mL round-bottomed flask equipped with a condenser, a stirrer bar, and a thermo-meter.

The mixture was heated to 90 °C. A mixture of 3.58 mL of 37 wt% formalin and 20 mL of deionized water was added dropwise to the flask. After being stirred for 3 h, the solution was acidified with 1 M hydrochloric acid to around a pH of 5.5 to 6 to precipitate the target product KL/DAEA/DETA/F or KL/DETA/F. The solid was obtained by filtration, washed with cooled deionized water, dried at 50 °C (Fig. 4), and characterized by elemental analysis and FT-IR. The nitrogen content and solubility of the synthesized samples are listed in Table 1.

Characterization techniques

Elemental analysis was carried out with an elemental analyzer (Elementar Vario EL Ⅲ, Germany) instrument. About 5 mg of sample was placed in a tin boat and analyzed using helium as the carrier gas at a flow rate of 200 mL·min^{-1}. Combustion was carried out at 1150 °C, and the reduction tube was maintained at 850 °C.

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

^{1}H-NMR spectra were recorded in $CDCl_3$ at room temperature on a Varian INOVA spectrometer operating at 600 MHz.

Surface tension measurements were carried out with the ring method using a JK99A Tensiometer (Powereach Instruments, China). Deionized water (electrical resistivity = 18.2 MΩ·m^{-1}) was used in this measurement. The samples were dissolved in a dilute HCl aqueous solution, and the pH was adjusted to 2.0. The solution was then diluted to different concentrations with 0.01 M HCl. Thirty minutes after the sample was added to a measurement dish, the surface tension was measured. Measurements were performed in triplicate, and the average values were calculated. Critical micelle concentration (CMC) values were determined at the discontinuity point on a plot of surface tension *vs*. logarithm of concentration.

Measurement of HLB values and foamability were performed as follows: Standard oil samples with HLBs of 10, 11, 12, 13, 14, and 15 were prepared by mixing of a set amount of bean oil (HLB=6) with turpentine oil (HLB=16). Then, 2.0 g of sample was heated to dissolution in dilute hydrochloric acid, adjusted to a pH of 2, and diluted to 200 mL with 0.01 M hydrochloric acid. Next, 20 mL of standard oil samples with HLBs of 10, 11, 12, 13, 14, or 15 were added to a 100-mL mixing cylinder with stopper. Then, 20 mL of the solution of samples mentioned above was added to each cylinder. The stopper was covered, and the cylinder was shaken from top to bottom violently for 5 times, then left to stand for 1 min; this procedure was performed 5 times, until the oil and water became a homogeneous mixture. The water separation time was recorded immediately when the volume of water was exactly 10 mL. The volume of foam initially and after being left standing for 5 min was also recorded.

Zeta potential was measured at room temperature using a Zetasizer (Nano-ZS, Malvern Instruments, UK) which works on the principle of dynamic light scattering. The samples solution was prepared following the above-mentioned procedure in surface tension measurements, then diluted to different concentration with 0.01 M HCl for analysis. This dilution factor was chosen to ensure that the maximum concentration used for the measurement was $\leqslant$ 10 mg·mL^{-1} in line with the manufacturer's specification. Measurements were performed in quadraplicate, and the average values were calculated.

RESULTS AND DISCUSSION

Preparation of Cationic Amphiphilic KL Derivatives

From the FT-IR spectra of DA, DC, and DAEA (Fig. 2), the peak that appeared from 2500 to 3500 cm^{-1} was assigned to the stretching vibrations of -OH, and the peak at 1693 cm^{-1} was assigned to the C=O double bond stretching vibrations in DA. When DA reacted with $SOCl_2$ to form DC, the stretching vibration peaks of the -OH disappeared, and the C=O peak moved to 1788 cm^{-1}, while some new peaks assigned to stretching vibrations of C-Cl at 775 and 723 cm^{-1} appeared. In comparison with DC, DAEA had a new peak that was assigned to N-H stretching vibration at 3331 cm^{-1}, and the C=O peak moved to 1635 cm^{-1}. At the same time, the peaks at 775 and 723 cm^{-1} disappeared.

Figure 3 shows the FT-IR spectra of KL, KL/DAEA/F, KL/DETA/F, and KL/DAEA/DETA/F. After KL was modified by DAEA, the absorption peaks in KL/DAEA/F at 3400, 2935, 1460, 1370, and 1082 cm^{-1} became more pronounced. When KL/DAEA/F or KL was further reacted with DETA and F, the peaks at 3400 cm^{-1} increased significantly, peaks at 2935, 1460, and 1081 cm^{-1} also increased noticeably, and the peak at 815 cm^{-1} disappeared, indicating that the Mannich reaction had been carried out on the aromatic nucleus C_5 site. The peak at 1658 cm^{-1} may be assigned to the stretching vibrations of C=N double bonds in imine that was formed by the condensations in which carbonyl groups on C_α in lignin reacted with diethylenetriamine (Fig. 1).

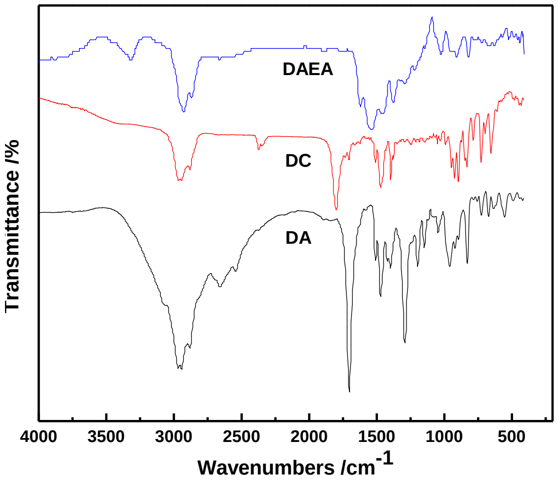

Fig. 2. FT-IR spectra of DA, DC, and DAEA

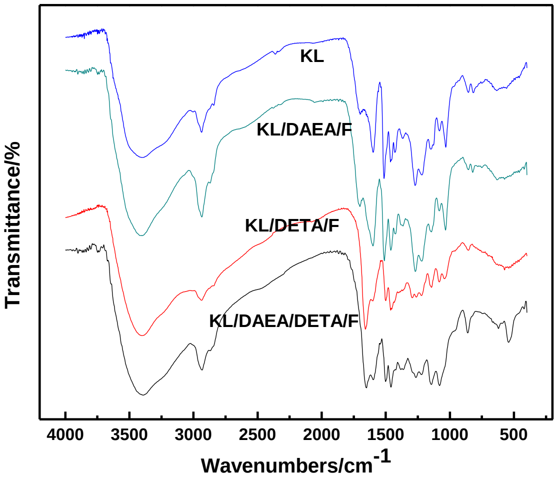

Fig. 3. FT-IR spectra of KL, KL/DAEA/F, KL/DETA/F, and KL/DAEA/DETA/F

DAEA was also characterized by ^1H-NMR. The attribution of the peaks is as follows (Fig. 4): δ /ppm: 7.10～6.86 (3H, 11Ar-H, 12Ar-H, 14Ar-CH), 6.41 (1H, NH), 3.33～3.29 (2H, 21CH_2), 2.83～2.81 (5H, 7CH_2, 15CH, 22CH_2), 2.31～2.13(4H, 6CH_2, NH_2), 1.79～1.51 (7H, 1CH_2, 2CH_2, 3CH_2, 5CH), 1.74～1.51 (3H, 20CH_3), and 1.49～1.20 (9H, 16CH_3, 17CH_3, 19CH_3).

The nitrogen contents of KL, KL/DAEA/F, KL/DETA/F, and KL/DAEA/DETA/F are given in Table 1. It can be seen that the nitrogen content was raised dramatically after the Mannich reaction had been carried out, which means the dehydroabietyl groups and diethylenetriamine groups were introduced into lignin by this reaction.

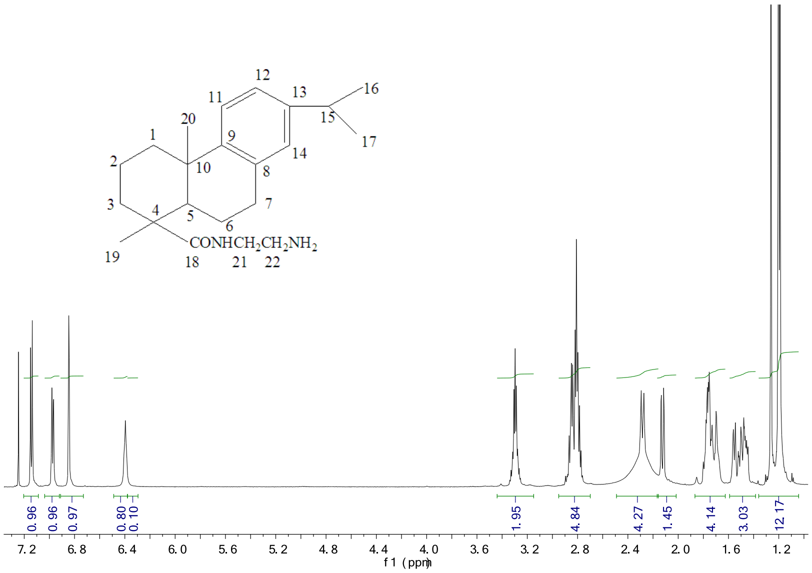

Fig. 4. 600 MHz ^{1}H-NMR spectrum of DAEA in $CDCl_3$

Table 1. Nitrogen Content in KL and Various Modified KLs

Samples	Molar ratio of charge	Nitrogen content (wt%)	Solubility (wt%)
KL	N/A	0.05	insoluble
KL/DAEA/F	n(KL):n(DAEA):n(F)=1:0.25:0.25	1.48	insoluble
KL/DETA/F	n(KL):n(DETA): n(F)=1:0.75:0.75	4.10	2.90
KL/DAEA/DETA/F	n(KL/DAEA/F):n(DETA):n(F)=1:0.75:0.75	3.66	2.10

Evaluation of Cationic Amphiphilic KL Derivatives

The basic surface physico-chemical properties of cationic amphiphilic KL derivatives were evaluated by solubility, surface tension, HLB values, foamability, and zeta potential. All measurements were performed at pH 2.0. This is because this modified derivative is intended for use as an asphalt emulsifier to produce asphalt emulsions. Under acidic conditions (pH > 2.0), aggregates such as granite *etc.*, usually have negative charges and the emulsifier has positive charges, so they can attract each other.

As shown in Table 1, KL and KL/DAEA/F were insoluble in water at pH 2.0, but KL/DETA/F and KL/DAEA/DETA/F had good solubility in the same conditions and could be used as cationic surfactants. This is attributed to the introduction of diethylenetriamine groups that can react with protons to form ammonium salts under acidic conditions. The solubility of KL/DETA/F was higher than that of KL/DAEA/ DETA/F, most likely because of the higher nitrogen content.

The surface tension of cationic amphiphilic KL derivatives decreased considerably with increasing concentration (Fig. 5). The surface tensions of 5 $g\cdot L^{-1}$ aqueous solutions of KL/DAEA/DETA/F and KL/DETA/F at pH 2.0 were 29.85 $mN\cdot m^{-1}$ and 45.62 $mN\cdot m^{-1}$, respectively, which shows that the former has much better surface activity. This is caused by the introduction of lipophilic dehydroabietic acid groups, which result in a more regular and compact arrangement of KL/DAEA/DETA/F at the air-water interface with increasing concentration. When the concentration was more than 5 g·L^{-1}, the surface tension did not decrease and remained nearly constant; the critical micelle concentration is therefore judged to be 5 g·L^{-1} for these cationic amphiphilic KL derivatives.

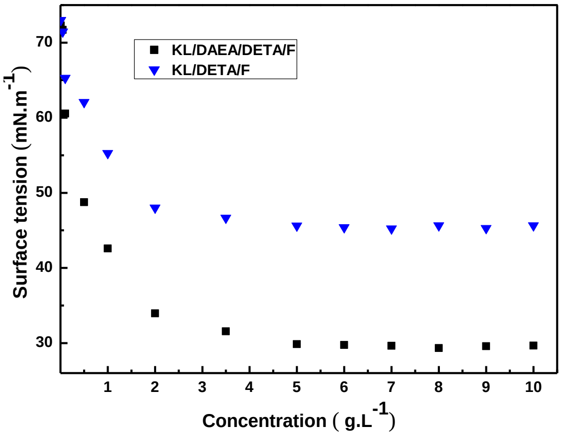

Fig. 5. Variation of surface tension with KL/DAEA /DETA/F and KL/DETA/F concentration at pH 2.0

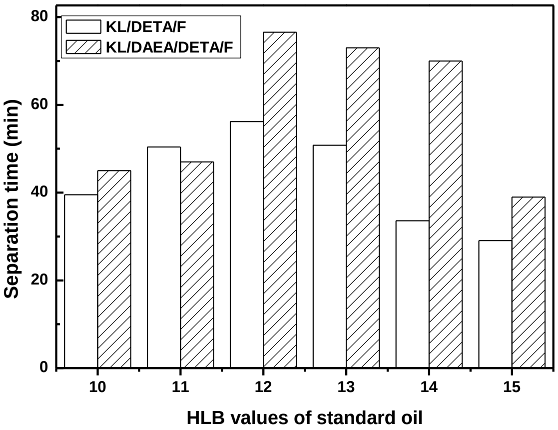

Fig. 6. Separation time of oil and water for standard oil emulsified by KL/DAEA/DETA/F and KL/DETA/F

The HLB value is an important parameter that gives an indication of how to use surfactants. HLB values of KL/DAEA/DETA/F and KL/DETA/F at pH 2.0 were measured by a standard oil mixture of bean oil and turpentine oil (Fig. 6). Standard oil samples with various HLBs were emulsified by KL/DAEA/DETA/F and KL/DETA/F aqueous solutions at the same concentrations. The separation time of oil and water was recorded. The HLB values of the surfactants should be equal to the HLB values of the oil samples that had the longest separation times. As shown in Fig. 6, both KL/DAEA/ DETA/F and KL/DETA/F had the same HLB value, *i.e.*, 12, which is suitable for W/O emulsion. This may be attributed to the fact that the content of dehydroabietic acid groups in KL/DAEA/DETA/F was so low that they imparted no obvious change in the HLB values. The separation time of KL/DAEA/DETA/F was longer than that of KL/DETA/F for the 12-HLB standard oil sample, which means that the former has a stronger emulsifying capacity.

The foamability of KL/DAEA/DETA/F and KL/DETA/F at pH 2.0 was measured by counting the foam volume when standard oil was mixed with a sample solution, both immediately afterwards and after leaving the foam to stand for 5 min. The modified KL derivatives had low foamability, and the foamability of KL/DAEA/DETA/F was slightly stronger than that of KL/DETA/F (Table 2).

Table 2. Foamability of Cationic Amphiphilic KL Derivatives

Samples	Initial foam volume (mL)	Foam volume after standing for 5 min (mL)
KL/DETA/F	7.5	6.0
KL/DAEA/DETA/F	11.1	8.0

Zeta potential of KL/DAEA/DETA/F in aqueous solution at pH 2.0 was explored at room temperature by varying its concentration (Fig. 7). From the figure, it can be seen that KL/DAEA/DETA/F had a positive charge due to formation of ammonium salts in acidic conditions. So, it can be used as a cationic surfactant, especially for an asphalt emulsifier. When the concentration was lowered to 2 $g{\cdot}L^{-1}$, the zeta potential increased significantly with the increasing of the concentration because the aggregates of KL/DAEA/DETA/F in aqueous solution at low concentration were unsaturated. As the concentration was continuously increased to 5 $g{\cdot}L^{-1}$, the zeta potential remained nearly constant, which indicates that the aggregates were saturated with KL/DAEA/DETA/F molecules, and micelles formed in the solution.

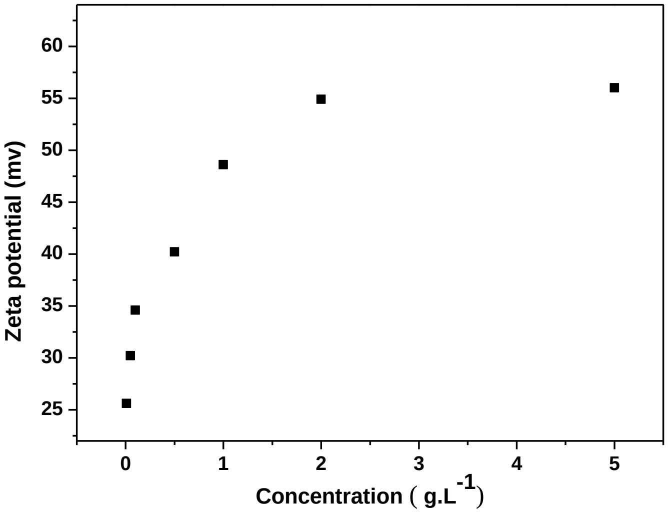

Fig. 7. Relationship between Zeta potential and the concentration of KL/DAEA/DETA/F in aqueous solution at pH 2.0

CONCLUSIONS

1. A novel lignin derivative with high surface activity (KL/DAEA/DETA/F) was prepared *via* the introduction of dehydroabietyl groups as lipophilic groups and diethylenetriamine groups as hydrophilic groups by the Mannich and ketone-amine condensation reactions.
2. Solubility, surface tension, HLB values, and foamability were used to evaluate the basic physico-chemical properties of the cationic amphiphilic derivative. It was found that the solubilities of KL/DAEA/DETA/F and KL/DETA/F were 2.10 and 2.90 wt% in aqueous solution at pH 2.0, respectively. The surface tensions of KL/DAEA/DETA/F and KL/DETA/F were 29.85 and 45.62 $mN{\cdot}m^{-1}$, respectively, at a concentration of 5.0 $g{\cdot}L^{-1}$. Both derivatives had HLB values of 12 and low foamability.
3. Zeta potential tests showed that KL/DAEA/DETA/F had a positive charge due to formation of ammonium salts in acidic conditions. So, it can be used as a cationic surfactant.

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