Surface-Active Properties of Hydrophobized Derivatives of Lignosulfonates: Effect of Structure of Organosilicon Modifier

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ABSTRACT: An investigation of regularities of surface-tension alterations in the aqueous solutions of lignosulfonate and aluminum-containing organosilicon oligomer (olygoheterosiloxanolates) reaction mixtures revealed that modification with oligomers can be used for the regulation of the surface activity of lignosulfonates. High surface activity not only in acidic, but also in neutral and alkali media, is achieved using oligomers which consist of ethylsesquioxane and diethylsiloxane links. In this case, increasing hydrophobicity compensates the negative effects (increase of solubility and the Coulomb repulsion) of ionization of lignosulfonate acidic groups. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1013–1020, 2001

Key words: polymeric surfactants; lignosulfonates; organosilicon oligomers

INTRODUCTION

Lignosulfonates (LS), a water-soluble polydisperse polyelectrolyte, are formed in the process of cellulose manufacture by the sulfite method from wood or other plant raw materials.[1] The basic units of the polymer consist of C_6—C_3 structure moieties linked together by ether and carbon bonds. The LS macromolecule contains anionic groups of different kinds: sulfur-containing groups formed at the carbon atoms of propane chains, phenolic hydroxyl groups, carboxyl groups, and Mg or Na or Ca cations as counterions. Commercial LS consist of real LS and carbohydrates and ash admixtures. Nowadays, LS find wide application as technical surfactants with dispersing, stabilizing, and adhesive abilities.[2–4] In recent years, LS have been used as auxiliary substances for papermaking and paper coating.[5,6]

In general, hydrophilic properties of LS are determined by the presence of strongly acid sulfonic groups, while phenylpropane units are considered as hydrophobic moieties. Thus, the degree of sulfonation and molecular mass can be assumed as the main factors influencing LS adsorption onto the water–gas interface. It was found that LS surface activity is a complex characteristic strongly affected by the LS features—molecular masses, functionality, nature of the basic cation, and presence of carbohydrates and ash—and by external conditions—temperature, solvent polarity, presence of low-molecular electrolytes, etc.[7–10] Nowadays, the main problem of LS usage as a surfactant is the necessity to increase the range of their effective action by decreasing the dependence of their surface-active properties on varying external conditions and, especially, on media acidity.

Table I   Characteristics of Oligoorganosiloxanolates

Modifier	Organic Moiety at the Si Atom	Si Content (%)	Al Content (%)	Zn Content (%)
SIL-1	Ethyl	5.0	1.7	—
SIL-2	Ethyl	5.0	1.0	—
SIL-3	Ethyl	5.0	0.5	—
SIL-4	2,2-Diethylethyl	5.0	1.0	—
SIL-5	Ethyl	5.0	—	—
SIL-6	Ethyl	5.0	—	2.5

The present work developed our previous investigations aimed at generation of the background for purposeful alteration of LS efficiency as a surfactant. Thus, it has been proposed that LS macromolecules form polylayer adsorption covers at the water–air interface. The dependence of the LS surface activity on the monovalent counterion shell size and the possibility of a purposeful influence on the surface activity of LS by introduction of hydrophobic blocks via modification with silicon-containing oligomers, for example, oligomeric organosiloxanolates, have been established. The formation of polyelectrolyte complexes of LS–oligoaluminoorganosiloxanolates in aqueous solutions was shown.[9–13]

The main task of the present work was to elucidate the relationship between the structure of an oligoaluminoorganosiloxanolate used as a modifier and changes in the LS hydrophobicity and surface-active properties of the modified LS. To achieve this goal, surface-active organosiloxanolates containing an equal amount of silicon, but differing in the contribution of hydrophobic organic moieties (ethylsylsesquioxane links only or ethylsilsesquioxane simultaneously with diethylsiloxane ones) and the content of aluminum in their structure, were chosen as modifiers.

EXPERIMENTAL

Materials

Sodium LS with $\bar{M}_w = 42{,}800$ were obtained by ultrafiltration from commercial LS isolated from spent liquors after sulfite delignification of softwood. The sample contained less than 1% of carbohydrates, 1.23 mequiv/g of sulfonate groups, and 1.08 mequiv/g of phenolic hydroxyl groups.

The synthesis of organosiloxanolates (SIL) was performed based on the original technique developed by A. Shapatin and I. Demidov, coauthors of the present work. The main characteristics and structure moieties of the SIL used are shown in Table I and Figure 1. The oligoorganosiloxanolates without polyvalent metal in their structure (SIL-5) and containing zinc instead of aluminum (SIL-6) were synthesized to compare their influence on the LS surface activity with that of aluminoorganosiloxanolates.

The LS interaction SIL was carried out in aqueous media at room temperature in the range of the coreagents' mass ratio $\mathbf{n}$ = [SIL]/[LS] from 0.01 to1.0, as was described in detail elsewhere.[14] The polyelectrolyte complexes resulted from the interaction are called MLS in this article.

Methods

Twice-distilled deionized water was used for preparing the LS and MLS solutions. Hydrochloric acid or sodium hydroxide was used to adjust the pH level. Potentiometric titration of oligoorganosiloxanolates in aqueous media as well as pH value measurement were performed using a potentiometer "Radiometer" with a glass measuring electrode.
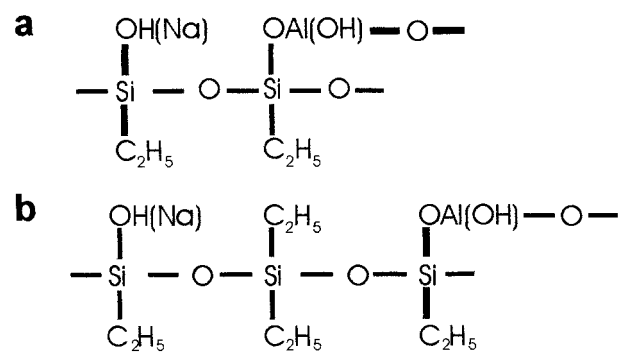
Figure 1 Structure fragments of oligoorganosiloxanolates containing (a) ethylsylsesquioxane moieties only or (b) ethylsilsesquioxane simultaneously with diethylsiloxane: (a) for SIL-1, -2, and -3; (b) for SIL-4.

The accuracy of the measurement was a ±0.01 unit of pH.

Before surface-tension measuring, the LS and MLS solutions were equilibrated in measuring cells for 24 h in accordance with ref. 9. The surface tension, σ, of the solutions was measured at 20ºC by the Wilhelmi method, using a sandblasted platinum plate with a perimeter of 5 cm. The measurement accuracy was $\pm 2 \times 10^{-4}$ N/m.

The behavior of LS and MLS on the water–air interface was characterized in terms of the work of adsorption, W_{ad}. The work of adsorption was calculated from the initial part of the surface-tension isotherms, using the formula $W_{ad} = RT \ln (\pi/C)_{C \to 0}$, where $\pi = \Delta\sigma = \sigma_{water} - \sigma_{solution}$ and C is the concentration of the polymer in the bulk solution.[15]

The hydrophilic–lipophilic properties of LS and MLS were estimated as described in ref. 8 in terms of the Gibbs free energy of the LS molecule transfer from the aqueous into the organic (ethyl acetate) phase: $-\Delta G^0_{aq \to oil} = G^0_{oil} - \Delta G^0_{aq} = -RT \ln C_{oil}/C_{aq}$, where C_{oil} and C_{aq} are the equilibrium concentrations in the ethyl acetate and water phases, correspondingly, after the equilibrium was achieved (15 days). LS concentrations were measured spectrophotometrically at $\lambda = 280$ nm.[16]

The formation of macromolecular aggregates in a bulk solution was studied using the laser light-scattering (LLS) method. LLS experiments were performed at the Centre of Molecular Diagnostic (Moscow, Russia) using a standard setup from EPIC equipped with an argon-ion laser (output power 135 mW at $\lambda = 514.5$ nm). Before the light-scattering experiments, the solutions were purified with a 0.5-μm pore-size Millipore PTFE filter. All measurements were carried out at 20 $\pm$ 0.1°C. In other respects, the details of the LLS experiment instrumentation were traditional.[17] From the static LLS data, the root-mean-squared z-average radius of gyration, R_G, was obtained by the Zimm plot method. In dynamic LLS, a hydrodynamic radius, R_h, distribution by the Stokes–Einstein equation was obtained.

Because the LS solutions under experimental conditions contain an equilibrium amount of nonassociated molecules, we need to subtract the scattering by nonaggregated LS molecules from the total scattering to characterize the aggregates. This has been done using EPIC software. The light-scattering experiments showed that the size distribution of the aggregates is well separated from that of the LS molecules. The number reverse to the flow time of 50,000 aggregates through the measuring unit of the LLS setup was taken as a characteristic of the effective concentration of aggregates in a solution, C_{eff}.

Table II   LS and MLS Hydrophobic Properties

| Sample	$-\Delta G^0_{aq \to oil}$ (kJ/mol)
LS	3.93
LS modified with following organosiloxanolates:	
SIL-1	2.36
SIL-2	2.55
SIL-3	2.70
SIL-4	2.00

The relative error is ±5%.

RESULTS AND DISCUSSION

LS and MLS Hydrophobic Properties

Comparison of free-energy values of macromolecule transition from the water phase to the organic one, $-G^0_{aq \to oil}$, showed (Table II) that MLS hydrophobicity increases when modifiers with ethylsesquioxane links (aluminoethylsiloxanolates) are changed for the oligomers with an increased share of hydrophobic organic moieties at the silicon atom (diethylaluminoethylsiloxanolates).

Formation of the macromolecular aggregates, that is, associative complexes, is a characteristic feature of the LS solutions.[16,18] The results of LLS experiments revealed that increase of the hydrophobicity of the LS macromolecule owing to the interaction with oligoheterosiloxanolates promotes association in the polymer acidic solutions. This process is pH-dependent. As the C_{eff} of the aggregates increases and their hydrodynamic radii grow as well (Fig. 2 and Table III), simultaneously, the ratio R_h/R_G increases (Table III), revealing an enlargement in the density of the associates' structure.[19]

The most distinct increase in the size of the macromolecular aggregates takes place with small quantities of the oligomer coreagent in the binary mixture, that is, at the ratio [SIL]/[LS] = 0.02 (Fig. 3). With increase of **n** (to 0.1 and higher), some decrease in the aggregate size is observed, and at the same time, these associative
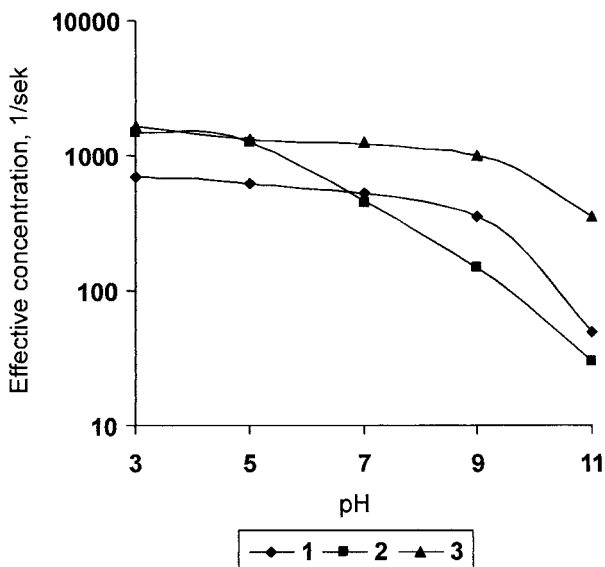
Figure 2 Influence of media acidity on the macromolecular aggregates' effective concentration in LS and MLS solutions (concentration 2.5 g/L) by LLS data: (1) LS; (2) LS–SIL-2; (3) LS–SIL-4. [SIL]/[LS] = 0.1.

complexes are characterized by a denser structure.

The data obtained reveal that the structure of the aggregates is strongly influenced by the coreagent ratios. At a small value of **n**, organosiloxanolate molecules attached to LS are randomly distributed at a considerable distance from one another and have no opportunity for self-association [Fig. 4(a)]. Owing to the polyelectrolyte nature of LS, their interaction with surface-active ionogenic organic compounds occurs cooperatively. With an increasing content of SIL molecules in the reaction mixture, the distance between the siliconorganic blocks changes, provid-

Table III   Dependence of the Size and the R_h/R_G Ratio of Aggregates in LS/MLS Dilute Solutions on the Oligoorganosiloxanolate Type

Sample	R_h (nm)	R_h/R_G
LS	93	1.2
LS modified with following organosiloxanolates:		
SIL-1	172	1.4
SIL-2	132	1.3
SIL-3	123	1.4
SIL-4	175	1.5

pH 5; coreagents ratio **n** = 0.1. The relative errors are R_h ±5% and R_h/R_G ±10%.
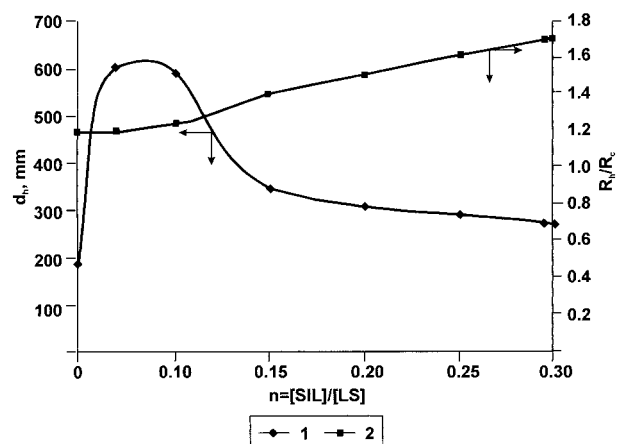
Figure 3 Influence of the LS and oligoorganosiloxanolate mass ratio in solutions (concentration 0.1 g/L) on the size and structural density of LS–SIL-1 macromolecular aggregates by LLS data: (1) average hydrodynamic radius, R_h; (2) R_h/R_G. pH 3.

ing the most favorable conditions for hydrophobic interactions of oligomer nonpolar parts. Intermolecular hydrophobic interaction has led to the compression of the aggregates. This reveals an increase in the density of the aggregates. It could be proposed that self-associates of SIL localize in the "emptiness" of LS macromolecular aggregates [Fig. 4(b)]. This model is confirmed by a decrease
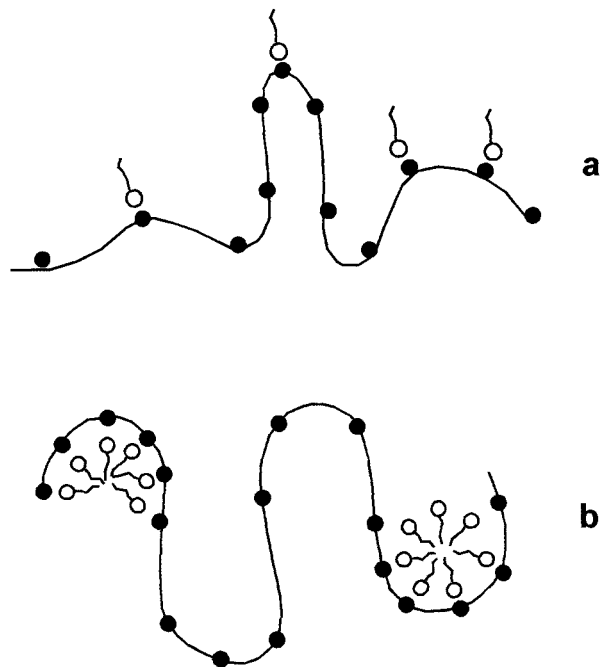
Figure 4 Schematic representation of the LS–SIL aggregates: (a) SIL]/[LS] < 0.1; (b) [SIL]/[LS] > 0.1.
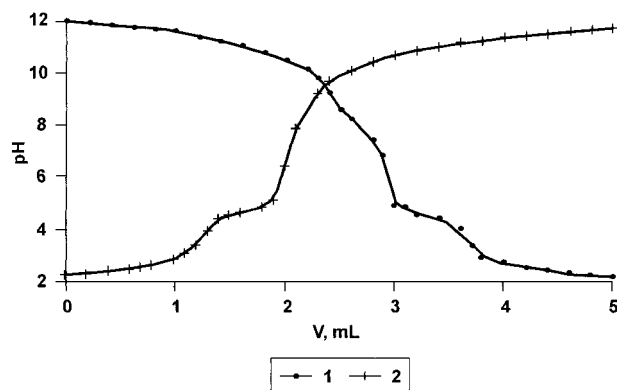
Figure 5 Potentiometric titration curves for SIL-1: (1) acid addition curve (0.1 **n** HCl); (2) base addition curve (0.1 **n** NaOH).

Figure 6 Potentiometeric titration curves for SIL-4: (1) acid addition curve (0.1 **n** HCl); (2) base addition curve (0.1 **n** NaOH).
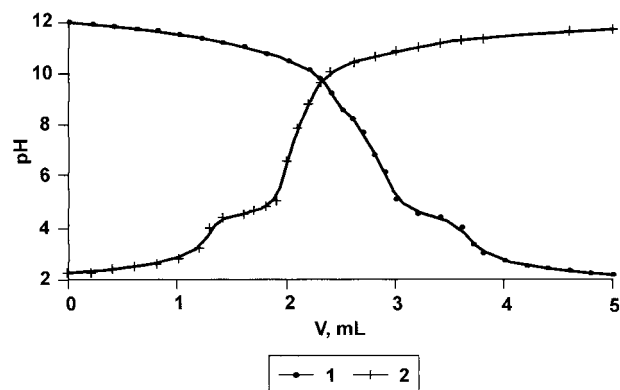
in the size of the aggregates with an increasing relative SIL amount (Fig. 3).

An increase in the amount of aliphatic groups at the silicon atom in the organosiloxanolate coreagent improves hydrophobic interactions, stabilizing mixed aggregates of LS and SIL. As can be seen from the comparison of the results for MLS with ethylsesquioxane moieties (SIL-2) and MLS with both ethylsesquioxane and diethylsiloxane moieties (SIL-4), the increasing hydrophobicity of organosiloxanolate blocks strengthens the association effectively. In the case of SIL-4 as a coreagent, not only the effective concentration of the aggregates enlarges, but also their stability in the alkali media increases (Fig. 2).

Influence of Interaction with Organosiloxanolates on Surface-Active Properties of LS

LS and SIL ions have charges of the same sign in alkaline media of the pH 9–11 range, whereas, in the acidic media, SIL and LS are charged oppositely, due to the presence of the aluminum atom in the SIL structure. The poteniometric titration curves for organosiloxanolates are shown in Figures 5 and 6. For aluminoethylsiloxanolates SIL-1, -2, and -3, these curves are identical (Fig. 5). The first equivalent point on the acid addition curves at pH 8.5 (SIL-1, -2, and -3) and 9.2 (SIL-4) corresponds to the siloxanolate group's dissociation. This point partly overlaps the second equivalent point, which corresponds to titration of the alkali excess, which is especially noticeable on the base addition curves. The third equivalent point (pH 3.7) in the acidic media can be assumed as the dissociation of bonds at the aluminum atom.

In the acidic media, the isotherm of the LS solutions' surface tension under the influence of

aluminoorganosiloxanolates shifts to the area of σ lower values (Fig. 7). As was mentioned, the oligoorganosiloxanolates under investigation also depress the water-surface tension to some extent (Fig. 8). Analysis of the surface-tension isotherms for acidic solutions (pH $\leq$ 5) of the LS–SIL mixtures showed a synergetic depression of the surface tension in the definite range of the components' ratio, namely, at $0.02 \leq$ **n** ≤ 0.1. The isotherms $\sigma = f(c)$ were used to determine the values of the surface activity, $-d\sigma/dc$ (Fig. 9). A sharp increase in the $-d\sigma/dc$ values in the narrow range of the ratio [SIL]/[LS] alteration proves the suggestion about statistical binding of oligomer molecules with LS at low values of **n**, which was made on the basis of the LLS data. In the range of the coreagents' ratio $0.02 \leq$ **n** ≤ 0.1, the surface activity increases due to the local increase of the
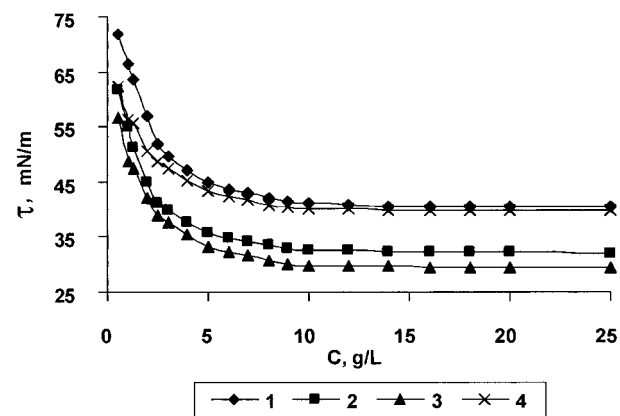
Figure 7 Surface-tension isotherms $\sigma = f(C)$: (1) LS; (2) LS–SIL-1; (3) LS–SIL-4; (4) LS–SIL-3. pH 4.5, [SIL]/[LS] = 0.1.
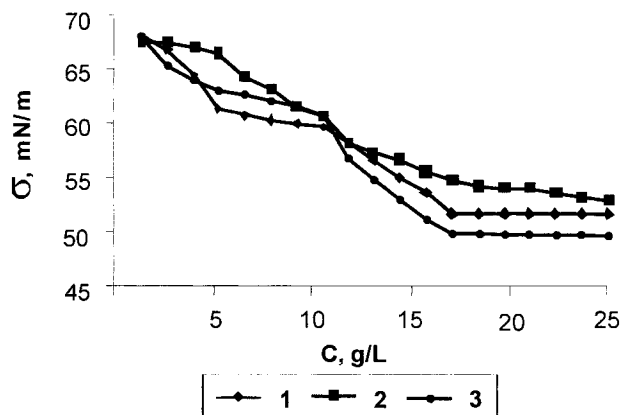
Figure 8   Surface-tension isotherms $\sigma = f(C)$ for organosiloxanolates solutions: (1) SIL-1; (2) SIL-3; (3) SIL-4.

LS macromolecule hydrophobicity. Hydrophobic blocks of olygosiloxanolates, set up at a considerable distance from one another, work as "floats," trying to push away aggregates from the water into the less polar air media [Fig. 4(a)].

Decrease in the surface activity at the higher degrees of modification (Fig. 9) confirms, that at the ratio **n** > 0.1, SIL molecules, interacting with LS, are being localized, forming self-micelles, preferably inside the structures formed by the LS macromolecules. The surface activity of the modified LS at such degrees of SIL binding obviously will trend to the values characteristic of the original LS [Fig. 4(b)].

The hydrophobization of the LS macromolecule and compensation of the polyelectrolyte charge in acid media in the presence of SIL provides a considerable decrease of the area taken by MLS in the adsorption layer (Table IV). Obviously, the decrease in the adsorption-area values is connected to the increasing participation of the polymer associates in the formation of an adsorption layer, when only part of the molecules adsorbed is touching the interface directly. The work of adsorption for MLS increased approximately 1.5 times, showing the surplus of energy from the transfer of MLS molecules from the bulk solution onto the water–air interface, as compared with the same for LS (Table IV).

The data obtained, taken as whole, show that there is some kind of optimal hydrophobicity when the surface activity of the modified LS reaches the highest value. Along with that, hydrophobicity is not the single factor influencing their ability to depress the surface tension. Obviously, the considerable influence has changed the charge and conformation of the molecules in media of different acidity and the stability of polyelectrolyte complexes LS–SIL as well.

Compared to the initial LS, the σ values are higher for the number of modified products, at a water solution pH higher than 5 (Fig. 10). This can be caused by the ionization of siloxanolate groups, which increases the hydration of modified LS at higher pH values.

In the absence of the aluminum atom in the SIL molecule (SIL-5), the surface activity of the MLS is considerably decreased, in the whole range of LS concentrations and pH (Fig. 10). With the growth of aluminum contents from 0.5 to 1.7% in SIL-3 and SIL-1, respectively, σ depression ($\Delta\sigma_{LS+SIL} = \sigma_{water} - \sigma_{LS+SIL}$) increases by 10–12 mN/m in the acidic solutions, compared to $\Delta\sigma_{LS}$ (Fig. 7). The presence of a bivalent metal (Zn) instead of aluminum (SIL-6) in the SIL structure influences insignificantly the surface activity of the LS even in the acidic media (Fig. 10). The favorable influence of the aluminum on the surface activity of LS is obviously caused by the strengthening of the LS:SIL complexes due to the redistribution of the electron density between ar-
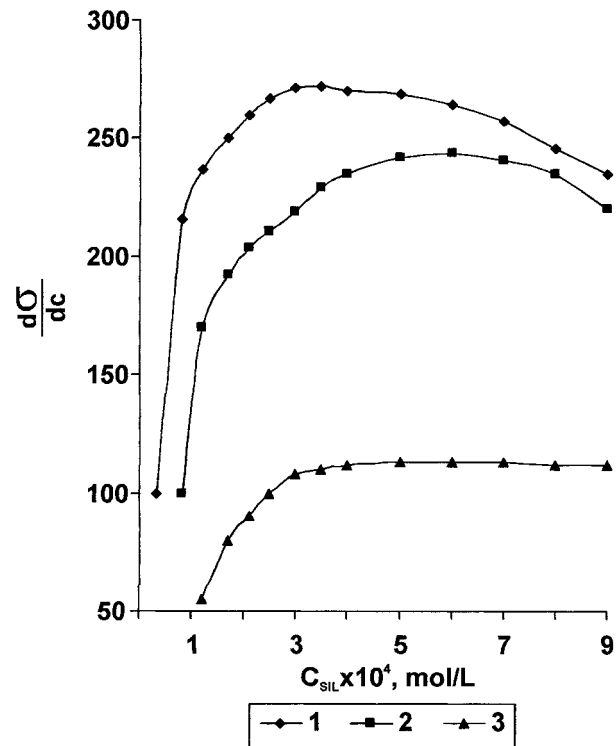
Figure 9   Surface activity of MLS (modifier SIL-4) at LS concentration: (1) 0.04×10^{-3} M; (2) 0.1×10^{-3} M; (3) 0.15×10^{-3} M. C_{SIL}, concentration of SIL-4.

Table IV   Characteristics of LS and MLS Adsorption on the Water/Air Interface

Sample	Adsorption, $\Gamma_\infty \times 10^6$ (mol/m^2)	Adsorption Area per Monomer, S_∞ (Å^2)	Work of Adsorption, W (kJ/mol)
LS	1.2	138	17.3
LS modified with following organosilaxanolates:			
SIL-1	2.9	78	25.9
SIL-2	2.4	96	24.1
SIL-3	1.7	112	20.5
SIL-4	3.8	44	27.2

Water phase pH 5.0.

omatic structural fragments and unfilled 3s and 3p orbitals of the aluminum.[20]

In acidic media, the presence of aluminum in the structure of SIL provides an increase of the number of the positively charged centers in the lignin macromolecule, which weakens the interaction with H_3O^+ ions and improves the adsorption of macromolecules on the interfaces. The presence of diethylsiloxane links together with ethylsilsesquioxane in the structure of the organosilicon olygomer provides the most surface activity of MLS (LS–SIL-4) and leads to nonadditive depression of σ, not only in acidic but also in neutral and alkalescent solutions (Fig. 10). This is obviously connected with the fact that LS hydrophobicity, achieved by modification with the SIL-containing ethylsilsesquioxane and diethylsiloxane moeities, is not considerably changed by LS ionization. Besides, dissociation of the siloxanolate groups is observed for aluminoethyldiethylsiloxanolate at higher pH (9.2) as compared with aluminoethylsiloxanolate (8.5). This also widens the pH range in which the high surface activity of MLS is being maintained.
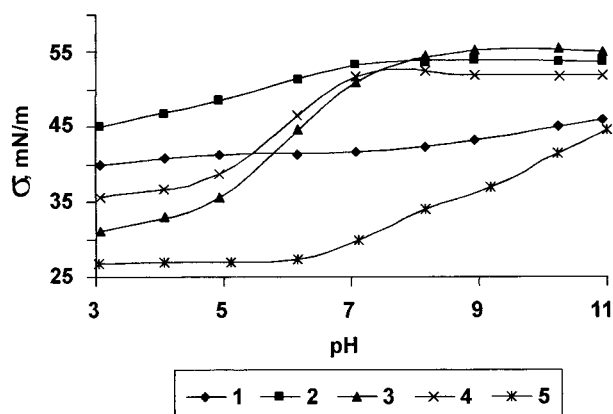
CONCLUSIONS

The surface activity of LS can be regulated by modification with aluminum-containing oligoorganosiloxanolates. Modification products formed in the acidic media at the mass ratio of LS and oligomers $0.02 \leq \mathbf{n} \leq 0.1$ have higher hydrophobicity if compared to the nonmodified LS and exhibit synergetic σ depression overall all the surface-tension isotherm. The highest surface activity not only in acidic but also in neutral and alkalescent solutions is achieved using the oligomer, whose higher hydrophobicity compensates the negative effects of ionization (increase of solubility and the Coulomb repulsion) of coreagent acidic groups.

Figure 10   Influence of pH on surface tension of LS and MLS solutions: (1) LS; (2) LS:SIL-5 (see Table I); (3) LS:SIL-3; (4) LS:SIL-6; (5) LS:SIL-4.

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