
PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Bulk and Surface Properties of Lignosulfonic Acids and Their Salts

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Abstract—Results of a study of the influence exerted by the cation composition on the bulk and surface properties of modified lignosulfonates are reported. It was found that the dissolution of lignosulfonic acids is accompanied by dissociation and conformational transitions of macromolecules, which leads to concentration of molecules of lignosulfonic acids in the solution bulk and, as a consequence, to a substantial increase in the surface tension.

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In processing of sulfide raw materials by autoclave techniques, water soluble derivatives of lignin, technical-grade lignosulfonates (LSs), are used as surfactants to remove films of elementary sulfur from the surface of minerals. Being a waste from the sulfite cooking of wood, lignosulfonates are characterized by unstable quality parameters and poor efficiency in application [1]. The level reached in the theoretical understanding of the colloidal-chemical behavior of lignosulfonic acids and their salts gives no way of developing a unified approach to assessment, prognostication, and control of their surfactant properties. Systematic studies in this area will make it possible to find parameters determining the efficiency of LS application and substantiate methods for modification of their structure, which could improve their surfactant and, consequently, consumer properties.

The goal of our study was to examine the bulk (electrical conductivity, degree of dissociation, pH, and optical density) and surface (surface tension at the l–g interface) properties of a number of lignosulfonic acids and their salts.

EXPERIMENTAL

As starting samples served lignosulfonate from Solikamsk pulp-and-paper combine (LA no. 1) and also

the low-molecular (LS no. 2) and macromolecular (LS no. 3) fractions of lignosulfonates isolated by preparative ultrafiltration (1.5 MPa, 303–308 K) from industrial sulfite waste liquors from Krasnokamsk and foreign (Ligno Tech) pulp-and-paper plants. The mass-average molecular masses of the samples were 16 900, 9250, and 4630 a.m.u. for LS nos. 1, 2, and 3, respectively. The results of an elemental analysis of the samples are listed in Table 1. The physicochemical properties of solutions of all the samples (acid-base, associative-dissociative, and redox transformations in solutions) are described in [2, 3].

The capacity of lignosulfonates for exchange of cations was used to obtain LS samples with about the same component composition and molecular-mass distribution. It should also be noted that, when determining the set of cations in the composition of the lignosulfonates, we were based on their being represented in the sludge from the autoclave leaching of zinc concentrates and technical-grade sulfite waste liquors supplied by various pulp-and-paper plants.

In the first stage, the lignosulfonates in three samples were converted to the H-form (LSA no. 1, LSA no. 2, LSA no. 3). For this purpose, their solutions ($c = 1.28 \text{ g dm}^{-3}$) were passed through column packed with a KU-2 cation-exchange resin in the H-form. In the second stage, a solution of lignosulfonic acids (LSAs) was passed through

a cation-exchanger in the Mn^{+} -form, where $Mn^{+} = Na^{+}$, NH_4^{+} , Ca_2^{+} , Zn_2^{+} , Fe_3^{+} . The monitoring was performed by spectral and potentiometric analyses of samples periodically taken in the course of the process. The pH values of the solutions at the inlet and outlet of the column varied from 4.5–5.0 to 2.0–2.6, respectively.

The bulk and surface properties of the lignosulfonic acids and their salts were determined under isothermal conditions (293 K), with the concentrations of the modified samples varied within the range 0–0.32 g dm⁻³, by measuring the electrical conductivity κ ($\mu S\ cm^{-1}$), pH, optical density D , and surface tension σ (J m⁻²) of the solutions at the l–g interface (method of the capillary rise in the level of a fluid [4]).

RESULTS AND DISCUSSION

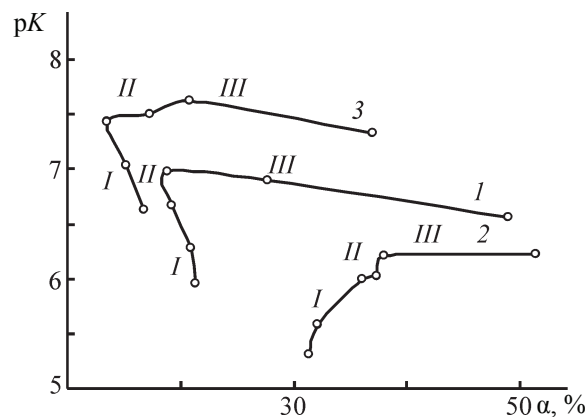
Lignosulfonic acids and their salts containing methoxy, phenolic, carbonyl, sulfonic, and other hydrophilic groups possess properties of polyelectrolytes [5]. Polyelectrolyte solutions are discrete systems in which microscopic volumes are limited by the size of macromolecular coils. Each macromolecular coil bears a charge of a certain sign. A local charge accumulation creates a strong electrostatic field around a macroion. As a result, a considerable part of counter ions is retained near the macroion by electrostatic attraction forces. The appearing electrostatic potential of the macroion determines the specific properties of polyelectrolytes [6].

Physicochemical Properties of Lignosulfonic of Acids

Analysis of electrical conductivity (Table 2) of solutions with various contents of lignosulfonic acids indicates that easily dissociable groups predominate in the low-molecular variety LSA no. 2.

The calculated degrees of dissociation (α , %) [7] of LSAs in solutions for the samples under study are listed in Table 2.

The degree of dissociation decreases with increasing molecular mass of lignosulfonic acids. In isoconcentration (0.01 g dm⁻³) solutions of LSA no. 1, LSA no. 2, LSA no. 3, it was, respectively, 51, 49, and 37%, in agreement with the conclusions made in [8]. The authors of [8] note that sulfonic groups in macromolecular Las are less susceptible to hydration due to the formation of a developed 3D network in solutions; the localization of acid groups



pK Value vs. the degree of dissociation, α , of lignosulfonic acids. LSA: (1) no. 1, (2) no. 2, (3) no. 3. (I, II, III) for explanations, see text.

in the internal structure restricts their accessibility and creates steric hindrance to development of hydrolysis processes. The latter accounts for the ambiguous variation of the pH value of LSA no. 3 solutions (Table 2).

The ionization of polyelectrolytes is accompanied by a cooperative conformational transition of molecular chains, i.e., by a sharp change in the shape of macromolecules in solution [9], which is confirmed by the curves plotted in the pK– α coordinates in the figure. Three portions can be distinguished in the curves: (I) initial portion of a steep rise in pK, which corresponds to the ionization of a structured form of LSA; (II) portion corresponding to the conformational transition, i.e., the rise in pK with increasing charge on the chain is compensated for by the unfolding of the chain and decrease in the linear charge density. In the case of the technical-grade sample LSA no. 1, this portion is somewhat smoothed because of the presence of different fractions; and (III) gradually sloping part of the curve, which corresponds to the ionization of macromolecules in the unstructured form.

Replacement of the cation in the sulfo group of a lignosulfonate and the resulting development of dissociation processes and conformational transitions changes the surface activity of macromolecules. The quantitative dissociation, more characteristic of lignosulfonic acids, compared with the salts from which they are obtained, favors liophilization and concentration of the acids in the solution bulk, with the resulting substantial increase in σ_{l-g} (Table 2). The rise in σ_{l-g} is also associated with the specific capacity of the H^{+} cation to coordinate around each of the interacting ions different numbers of water molecules not only due to the electrostatic interaction,

Table 1. Elemental composition of starting lignosulfonate samples

Element	Content, %, in indicated LS		
	no. 1	no. 2	no. 3
C	33.9	29.0	41.7
O	46.8	54.5	38.2
S	9.5	5.5	5.4
Na	5.7	6.6	0.8
K	0.18	0.04	–
Mg	0.80	–	–
Ca	–	–	3.0
The rest	3.12	4.36	10.9

but also via hydrogen bonds, with the result that LSAs are more strongly drawn by water molecules into the bulk of a solution [10].

Physicochemical Properties of Lignosulfonates

Na⁺, NH₄⁺, Ca²⁺, Zn²⁺, Fe³⁺

Sulfite-cellulose plants of the pulp-and-paper industry manufacture sodium, sodium–calcium, calcium–ammonium, ammonium, and magnesium salts of lignosulfonic acids. The cation composition of lignosulfonates strongly affects their physicochemical and consumer properties [11].

The physicochemical studies included determining the surface tension σ , electrical conductivity κ , pH value, and optical density D of solutions with various concentrations ($c_{\text{MLS}} = 0.01\text{--}0.32 \text{ g dm}^{-3}$) of modified lignosulfonates. The quantitative content of the above-specified cations

Table 2. Selected physicochemical properties of solutions of lignosulfonic acids

LSA	$c, \text{ g dm}^{-3}$	pH	$\sigma \times 10^{-3}, \text{ J m}^{-2}$	$\kappa_{\text{sp}}, \mu\text{S cm}^{-1}$	$\alpha, \%$
no. 1	0.01	4.7	59.3	18.8	48.9
	0.02	4.5	62.2	21.3	27.7
	0.04	4.1	–	29.0	18.9
	0.08	3.7	66.5	59.0	19.2
	0.16	3.3	69.2	128.8	20.9
	0.32	3.0	70.9	262.5	21.3
no. 2	0.01	4.8	76.7	10.0	51.4
	0.02	4.6	76.7	16.0	38.0
	0.04	4.0	–	29.0	37.3
	0.08	3.6	75.2	64.0	36.0
	0.16	3.4	73.8	100.0	32.1
	0.32	3.2	75.2	195.0	31.3
no. 3	0.01	4.5	78.1	4.8	37.0
	0.02	4.8	78.1	5.4	20.8
	0.04	3.4	–	9.0	17.3
	0.08	3.5	79.6	14.0	13.5
	0.16	3.7	81.0	31.5	15.2
	0.32	3.3	81.0	70.0	16.8

in the modified products (MLSs) was found by chemical analysis [12].

A decrease in the quantitative content of cations in the modified products was observed as the molar masses the lignosulfonates became smaller. The lignosulfonates had the highest capacity for the calcium cation, and the lowest capacity, for iron(III) ions. It was found that, as the rate at which solutions of lignosulfonic acids through the sorbent saturated with iron cations was raised (in the second stage) the content of a metal in the samples slightly decreased (Table 3).

At comparable concentrations, the optical density of the solutions became higher with increasing degree of oxidation of cations in the low-molecular variety LSA no. 2. In the same order of variation of the charge of cations (with the exception of Fe^{3+}), a decrease in the electrical conductivity was observed (Table 4). Judging from the pH value, the values of the electrical conductivity of solutions of iron lignosulfonates are overstated because the solution contains hydroxonium ions formed as a result of hydrolysis of Fe^{3+} ions. A similar manner of variation of the electrical conductivity was observed in solutions of the technical-grade sample MLS no. 1. No significant differences were observed in the optical density of the solutions in relation to the nature of a cation in the macromolecular variety MLS no. 3.

The increase in the optical density and the simultaneous decrease in the electrical conductivity in solutions of low-molecular lignosulfonates of iron, zinc, and calcium is accounted for by the ability of these cations to form chelate complexes with lignosulfonate ions; as noted in [13], this is accompanied by an increase in their molecular masses and by the resulting decrease in mobility.

The lowest pH values are observed for solutions of iron LS; the pH value steadily decreased as their concentration was raised at stabilized at 4.1–4.8 at $c > 0.15\text{--}0.20\text{ g dm}^{-3}$. A slight increase in pH was observed as the concentration of low-molecular and macromolecular LS of ammonium was raised. Changing the concentration of low-molecular MLSs of sodium, calcium, and zinc hardly affects the pH of their solutions, whereas in the presence of their macromolecular analogs (MLS no. 3), the pH value decreased as their concentration became higher.

A study of the surface activity of the modified samples demonstrated the following.

(1) Among the low-molecular MLS no. 2 under study, the highest surface activity at the l–g interface ($\sigma = 0.05\text{ J m}^{-2}$) was observed for varieties with singly charged cations in their composition (Na^+ , NH_4^+). The

Table 3. Content of metals in modified lignosulfonate samples

MLS sample	Content of a metal, %		
	Ca	Zn	Fe
no. 1	17.3	12.2	6.6
no. 2	14.7	9.1	2.2
no. 3	20.5	14.4	11.2

maximum surface-active effect was recorded at their concentrations of $0.04\text{--}0.05\text{ g dm}^{-3}$ in solution; outside this range, the surface tension of the solutions slightly increased and stabilized at a level of $0.05\text{--}0.06\text{ J m}^{-2}$ at $c_{\text{MLS no. 2}} > 0.3\text{ g dm}^{-3}$. In the presence of low-molecular LSs of iron, calcium, and zinc, the opposite effect was observed: the surface tension of the solutions increased ($\Delta\sigma \approx 0.015\text{ J m}^{-2}$) even at their insignificant content in solutions ($c_{\text{MLS no. 2}} \approx 0.02\text{ g dm}^{-3}$, and at concentrations higher than 0.1 g dm^{-3} , the surface tension of their solutions stabilized at $0.075\text{--}0.080\text{ J m}^{-2}$. Thus, compared with the unmodified analog LS no. 2, the low-molecular ammonium lignosulfonate exhibits a higher surface activity at comparable concentrations in solution, with this difference becoming more pronounced as its higher quantitative content in solution. A similar manner in which the surface tension of solutions varied with the cation composition was also noted in the presence of technical-grade modified samples (MLS no. 1).

(2) The surface active macromolecular lignosulfonates of various cationic compositions (MLS no. 3) substantially differs from the characteristics of low-molecular and technical-grade modified samples. Irrespective of the type of a cation in their composition, the surface tension of solutions at the l–g interface increased, with this effect being the most in the presence of MLS no. 3 with singly charged cations.

The specific features of the surface activity of lignosulfonates, found in the present study to be determined by the nature of a cation in their composition, are in agreement with the data of [14]. As already mentioned, the effect of a cation consists in changing the molecular-mass distribution of lignosulfonates; the content of macromolecular fractions increases in the presence of cations with higher valence (Fe^{3+}). The surface inactivity of lignosulfonates with polyvalent cations and, in particular, Zn^{2+} , Fe^{2+} , and Fe^{3+} ions is accounted for by the ability of these cations to link chains of lignosulfonic acids via sulfo groups into coarse colloidal aggregates, with the latter circumstance making them inactive substances.

Table 4. Physicochemical characteristics of solutions of lignosulfonates with various cation compositions

c, g dm ⁻³	ae, μS cm ⁻¹					pH				σ × 10 ⁻³ , J m ⁻²					
	Na ⁺	NH ₄ ⁺	Ca ²⁺	Zn ²⁺	Fe ³⁺	Na ⁺	NH ₄ ⁺	Ca ²⁺	Zn ²⁺	Fe ³⁺	Na ⁺	NH ₄ ⁺	Ca ²⁺	Zn ²⁺	Fe ³⁺
MLS sample no. 1															
0.01	11.5	12.5	16.0	17.0	12.5	6.0	5.9	6.6	6.2	6.1	57.9	73.1	66.5	75.2	78.1
0.02	17.0	17.0	16.0	21.0	20.0	6.1	5.9	6.1	6.2	6.3	78.1	68.1	68.0	75.2	78.1
0.04	27.0	28.0	20.0	27.0	35.0	6.1	5.7	6.4	6.2	5.8	—	—	—	—	—
0.08	44.0	48.0	27.0	38.0	58.0	5.9	5.6	6.1	6.1	5.1	78.1	50.0	70.9	75.2	78.1
0.16	75.0	88.0	41.0	60.0	105.0	5.9	5.6	6.0	6.0	4.7	79.6	50.6	78.1	75.2	79.6
0.32	150.0	165.0	75.0	106.0	208.0	5.0	4.8	5.3	5.1	4.3	79.0	57.9	76.7	75.2	79.6
MLS sample no. 2															
0.01	55.0	18.0	9.0	6.5	8.5	4.0	4.6	4.9	5.7	4.3	60.8	53.5	66.5	78.1	78.1
0.02	45.0	13.0	11.0	7.8	9.8	4.0	5.4	5.3	5.2	5.1	70.0	62.2	70.9	78.1	76.7
0.04	53.0	14.0	16.0	12.0	17.5	3.9	5.6	5.4	4.9	4.6	—	—	—	—	—
0.08	74.0	15.0	24.0	18.5	32.0	3.8	6.0	5.2	5.0	4.0	65.1	60.8	65.1	76.7	79.6
0.16	85.0	44.0	38.0	29.0	60.0	3.8	5.8	5.2	5.0	3.7	73.8	75.2	76.7	79.6	78.1
0.32	123.0	80.0	68.0	58.0	123.0	3.0	5.6	4.5	4.6	3.5	76.7	76.7	78.1	78.1	79.6
MLS sample no. 3															
0.01	5.3	6.0	5.8	6.0	6.5	5.4	5.5	5.0	4.7	4.7	79.6	78.1	76.7	73.8	73.4
0.02	6.6	7.0	6.3	6.5	6.5	5.5	5.2	5.0	5.0	5.1	76.7	78.1	76.7	76.7	76.7
0.04	9.8	9.8	8.1	8.0	11.0	5.6	5.3	5.1	4.9	4.8	—	—	—	—	—
0.08	19.5	16.0	11.0	12.0	16.5	5.6	5.4	5.2	4.9	4.6	76.7	77.3	78.1	76.7	69.4
0.16	34.0	27.0	16.8	19.0	28.0	5.8	5.5	5.4	5.0	4.3	79.6	76.7	79.6	78.1	76.7
0.32	57.0	47.5	30.0	38.0	50.0	5.7	5.9	5.5	4.8	4.0	78.1	76.5	73.8	76.7	69.4

Thus, macromolecular modified lignosulfonates have a lower surface activity than the salts from which they are obtained.

CONCLUSIONS

(1) Changing the cation composition of lignosulfonates strongly affects their bulk and surface properties. The latter should be taken into account in their use in technological cycles, including that in autoclave leaching of sulfide materials.

(2) The dissolution of lignosulfonic acids is accompanied by dissociation and conformational transitions of macromolecules. In the process, the degree of dissociation of lignosulfonic acids decreases as their molecular mass increases and the solutions are diluted.

(3) The quantitative dissociation of lignosulfonic acids and the specific ability of the H^+ cation to coordinate water dipoles not only due to the electrostatic interaction, but also via hydrogen bonds favor liophilization and concentration of molecules of lignosulfonic acids in the solution bulk and, as a result, lead to a substantial increase in the surface tension σ_{l-g} .

(4) Ammonium lignosulfonates are notable for the highest surface activity ($\sigma = 0.05\text{--}0.06\text{ J m}^{-2}$) among the low-molecular modified (no. 2) and technical-grade (no. 1) lignosulfonates.

(5) Replacing the cation in modified macromolecular lignosulfonates (no. 3) makes them inactive.

(6) The data obtained can be used to prognosticate the behavior of lignosulfonates at phase boundaries. The cation-exchange process can be regarded as a way to modify technical-grade lignosulfonates.

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