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# PHYSICO-CHEMICAL ASPECTS OF SURFACE-ACTIVE PROPERTIES OF LIGNOSULFONATES

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### Annotation

The use of surfactants is a promising direction for accelerating the processes of destruction of pigment aggregates and stabilizing them in the volume of paints. The paper considers the study of the surface activity of paper industry waste - lignosulfonates. The processes of adsorption, dispersing and stabilizing activity of lignosulfonates have been studied. The established surface-active properties of lignosulfonates open up the prospect of their use in paint compositions as wetting agents.

**Keywords:** surfactants, lignosulfonates, adsorption, dispersing activity, particle stabilization, thermal stability, surface tension.

# БЕТТІК-БЕЛСЕНДІ ЗАТТАРДЫҢ ФИЗИКА-ХИМИЯЛЫҚ АСПЕКТІЛЕРІ

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### Андатпа

Беттік-белсенді заттарды қолдану пигмент агрегаттарының бұзылу процестерін жеделдету және оларды бояулар көлемінде тұрақтандыру үшін перспективалы бағыт болып табылады. Жұмыста қағаз өнеркәсібі қалдықтарының беттік белсенділігін - лигносульфонаттарды зерттеу қарастырылады. Лигносульфонаттардың адсорбция, дисперсті және тұрақтандырушы белсенділігі зерттелген. Лигносульфонаттардың белгіленген беттік-белсенді қасиеттері оларды лак-бояу композицияларының құрамында суландырғыш ретінде пайдалану перспективасын ашады.

**Түйінді сөздер:** беттік-белсенді заттар, лигносульфонаттар, адсорбция, диспергирлеуші белсенділік, бөлшектерді тұрақтандыру, термостабельділік, беттік керілу.

# ФИЗИКО-ХИМИЧЕСКИЕ АСПЕКТЫ ПОВЕРХНОСТНО-АКТИВНЫХ СВОЙСТВ ЛИГНОСУЛЬФОНАТОВ

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**Аннотация**

Использование поверхностно-активных веществ является перспективным направлением для ускорения процессов разрушения агрегатов пигмента и стабилизации их в объеме красок. В работе рассматривается изучение поверхностной активности отходов бумажной промышленности - лигносульфонатов. Изучены процессы адсорбции, диспергирующей и стабилизирующей активности лигносульфонатов. Установленные поверхностно-активные свойства лигносульфонатов открывают перспективу их использования в составе лакокрасочных композиций в качестве смачивателей.

**Ключевые слова:** поверхностно-активные вещества, лигносульфонаты, адсорбция, диспергирующая активность, стабилизация частиц, термостабильность, поверхностное натяжение.

## Introduction

The use of surfactants is a promising direction for accelerating the processes of destruction of pigment aggregates and stabilizing them in the volume of paints. The production of paint and varnish materials (P&VM) is currently represented by a wide range of coatings with various protective and decorative properties. The insufficient amount of progressive scientific research in the field of creating paint compositions creates a prerequisite for a more in-depth analysis of paint compositions in order to modernize them. The product offered by the local market cannot always meet the needs of the consumer, which also indicates the need to develop optimal formulations of coatings with improved properties. The increase in operational characteristics can be achieved by introducing surfactants (surfactants) into the composition of paint and varnish compositions.

In the laboratory of physico-chemical research methods NKU, we have studied compounds with surface properties that have not yet been widely used in the creation of coatings. Such compounds include natural water-soluble sulfonates of high-molecular lignin (lignosulfonates) [3-6]. The variety of surfactants is classified according to their functional purpose, one of which is the wetting of pigment agglomerates. With regard to the relationship with the additive structure, the wetting process has been little studied, as well as the problems of the relationship between low-molecular surfactants and polymer solutions.

The surface activity of lignosulfonates is due to the diphilic structure of their molecules, which, along with ionic functional groups, contain uncharged polymer chains. The surface activity, as well as the colloidal-chemical properties of lignosulfonates, depend on their molecular mass distribution, functional, elemental compositions and structural (length and structure of the hydrocarbon radical, location of polar groups) characteristics of the macromolecule, as well as on external factors (temperature, electrolyte additives) [1-3].

According to [4;5], the fractions of lignosulfonates with a molecular weight of 10,000 - 50,000 containing 14-15% sulfite and about 10% carboxyl groups are characterized by the greatest surface-active effect; the above characteristics for lignosulfonates in sulfite alkalis are provided during the delignification of wood with a residue yield of 50-60%.

The most important feature of sulfonates is the increased ability to adsorb on the interface surfaces, accompanied by a change in the interfacial surface tension and, as a consequence, the characteristics of wetting, dispersion and emulsification. At the same time, conformational changes of their molecules in the adsorption layer play an important role in the development of adsorption processes [6].

The structure of the formed adsorption layers of lignosulfonates on the interface differs significantly from the structure of diphilic low molecular weight surfactants [7]. The decrease in the surface tension of solutions of high-molecular sulfonates (at the interface with air) is explained by the limited content of hydrophilic groups in them, in comparison with low-molecular varieties. In this regard, the static repulsive forces arising between the hydrophilic groups of high-molecular sulfonates are insignificant and, as a result, they are able to form a denser adsorption layer at the interface. With dense packing in the surface layer, the macromolecules of sulfonates are oriented into the aqueous phase by four to five monomeric units and have a complex spherical, close to ellipsoidal, conformation.

Among other features, the irreversible nature of the adsorption of lignosulfonates at the interphase boundaries and the duration of the establishment of adsorption equilibrium are noted. The surface tension of solutions of technical sulfonates is significantly influenced by concentration and temperature factors, as well as the conditions of delignification and subsequent processing operations of sulfite liquor. Thus, the products of sulfite-yeast mashobtained after the biochemical processing of lye are characterized by higher surface activity. The increased activity of the latter was explained by the presence of organic fatty acids in them (up to 0.2%) and at the same time the absence of a surface-active effect in previously purified (from carbohydrates and fatty acids) sulfite alkalis. The resulting surface-active effect of technical liquors, according to N.I. Afanasyev and G.M. Telysheva [8], along with lignosulfonates, sulfonated carbohydrates can also complement.

The available data on the effect of temperature on the surface tension of lignosulfonate solutions are very contradictory. The surface tension of the alkalis on the calcium base significantly and continuously decreased with an increase in temperature up to 363 K; at the same time, the presence of a minimum surface tension of calcium lignosulfonate solutions at 313 K. At the same time, anomalies in the surface tension characteristics of solutions observed under different temperature conditions are associated with changes in the composition and structure of sulfonates. According to the results of the study of the thermal stability of calcium lignosulfonate in neutral solutions, it was found that at 373 K, the sulfur content in its composition decreased by 9%, and the number of methoxyl groups did not change. When acidified ($C(H_2SO_4) = 14.6$ g/dm$^3$) solutions of the same sulfonate were treated under more severe temperature conditions (over 423 K), condensation processes developed by phenolic hydroxo groups with the formation of a three-dimensional structure and the cleavage of methoxyl groups from the macromolecule.

The study of the adsorption processes of lignosulfonates on solid-phase adsorbents is complicated by the variety of interactions of sulfonates in the bulk phase and the structures formed in the adsorption layer. The determining role of the polyelectrolyte composition of lignosulfonates and the characteristics of the solid surface in the implementation of the adsorption process by a variety of mechanisms - with the formation of hydrogen, coordination, Van der Waals, covalent bonds, as well as exchange interactions.

It is noted that phenolic hydroxogroups are responsible for the formation of hydrogen bonds, sulfogroups – for the formation of a double electric layer, aliphatic hydroxides and carboxyl groups, being electron donors – for the development of binding processes by the donor-acceptor mechanism.

According to the results of the study of the adsorption and dispersing action of sulfonates against kaolin, calcite, coal, gypsum and other solid-phase objects, it was found that lignosulfonates are adsorbed on the surface of kaolin particles, soil, quartz, alum and coal by the type of monolayer coating, occupying about 20% of the total surface of the particles; while from the standpoint of ensuring strength a significant role is assigned to the polar groups of solid-phase components.

I. Bragina and G.G. Belau established that the adsorption films of lignosulfonates on dolomite and hydrogetite are caused by chemical interaction with cations located in the lattice and on the surface of minerals, and on apatite by hydrogen bonds. The latter is also consistent with the nature of the change in the heat of wetting the surface of these minerals with solutions of sulfonates.

The stabilizing effect of lignosulfonates on calcite and kaolin suspensions is determined by the localization effect (reduction) of the surface charge of particles and practically does not depend on their molecular weight. The adsorption of sulfonates on the surface of particles (in particular cement) is carried out by an electrostatic mechanism due to the attraction of negatively charged sulfogroups and positively charged cement particles. With an increase in the concentration of lignosulfonates, the electrokinetic potential ($\xi$) decreases and at some concentration it takes a value equal to zero; under these conditions, the electrostatic repulsion forces between cement particles are minimal, which creates prerequisites for their aggregation. With a further increase in the concentration of sulfonates, the $\xi$-potential takes on a negative value and, at a certain value, provides a stabilization effect. From these positions, the increase stabilizing activity, in comparison with the initial sulfonates, of a number of modified sulfonates obtained by their oxidation (hydrogen peroxide) and sulfonation (sodium sulfite) is explained. The increase in the electrostatic attraction and adsorption capacity (by 30%) of the latter is consistent with the increased (in absolute value) values of their electrokinetic potential by 10 mV ($\xi$ =-30 mV).

The dispersing ability of sulfonates, from the standpoint of a protective colloid, is justified by Goring. Low-molecular fractions of lignosulfonates are capable of forming a dense adsorption layer on the surface of solid-phase dispersions at low concentrations, which causes their increased dispersing ability. For high-molecular fractions of sulfonates, in contrast to low-molecular varieties, protective functions are less characteristic, however, they have an increased ability to structure the system.

The high dispersing ability of low molecular weight sulfonates in suspensions was also noted in a number of later works. However, it was stated that high-molecular varieties at low concentrations exhibit mainly flocculating properties, and at elevated concentrations dispersing. The latter is consistent with an increase in the dispersing activity of sulfonates in the composition of sulfite liquors subjected to preliminary high-temperature treatment in an acidic medium. At elevated temperatures (453 K), due to the destruction of high-molecular sulfonates, the relative content of low-molecular fractions in their composition increased.

A number of features in the surface activity of lignosulfonates determined by the nature of the cation in their composition have been established. According to the work of G.M. Tarnarutsky, G.M. Telyshev effect of the cation is to change the molecular weight distribution of sulfonates, the content of high-molecular fractions increases in the presence of cations of greater valence (A1, Fe, Sg). When replacing the divalent cation in the composition of lignosulfonate with a monovalent one, their average molecular weight and the relative content of methoxyl groups in the molecule decreased.

With an increase in the valence of the cation in the composition of sulfonates, saturation of the adsorption layer is achieved at lower concentrations. The ability of a number of polyvalent cations, in particular $Fe^{2+}$ ions, to bind chains of lignosulfonic acids through sulfogroups into large colloidal aggregates was established, which, at excessive concentration, turned them into the category of inactive substances.

Based on the results of measuring the surface tension ($\sigma$) of lignosulfonate solutions with monovalent cations in the composition, as well as evaluating their surface activity and adsorption parameters at the liquid -gas interface, it was found that according to the maximum depression $\sigma$ they form a series: $H^+ > NH_4^+ > Li^+ > Na^+ > K^+ > Cs^+$. This sequence, with minor changes, is also preserved for other parameters of the adsorption process at the phase boundaries.

The relationship between the cationic composition and the surface activity of lignosulfonates, which are considered in the form of a hydrated microgel [(-$SO_3$·pN20) ($Me^+$-m($N_2O$))], is explained from the standpoint of changes in the polarizability of cations and the energy characteristics (heats) of adsorption and hydration processes. The ability of the cation to polarize the functional group in the lignosulfonate molecule to which it is directly bound depends on the degree of hydration of their water dipoles. For lignosulfonates containing alkali metal cations, there is an almost linear correlation in changes in thermodynamic parameters and surface activity. The potassium ion, characterized by lower values of the heat of hydration compared to sodium and lithium ions, coordinates a smaller number of water molecules and, as a consequence, the $SO_3^{2-}$ anion in the composition of the lignosulfonate molecule is hydrated more strongly than in the presence of the other two cations. In this regard, potassium lignosulfonate is more strongly drawn by water molecules into the bulk part of the solution and, as a result, is characterized by less surface activity than its sodium and lithium salts. For the same reason, potassium lignosulfonate molecules diffuse more slowly into the surface layer. Lithium lignosulfonates, due to the lower affinity of the hydrate complex to the surrounding water molecules, exhibit the greatest surface activity. Deviations for ammonium and hydroxonium lignosulfonates, according to N.A. Afanasyev, G.M. Telysheva, N.A. Due to their specific ability to coordinate water dipoles, namely, not only due to electrostatic interaction, but also through hydrogen bonds.

The area occupied by their molecules in the boundary layer also depends on the degree of hydration of the cation in the composition of lignosulfonates. With a decrease in the volume of the hydrate complex, the density of the electric charge per phenylpropane unit of the lignosulfonate molecule increases, which is accompanied by compression and a decrease in the area occupied by the lignosulfonate molecule in the monolayer.

The type of cation included in the macromolecule of lignosulfonates also affects the kinetics of the adsorption process. With an increase in the heat of hydration and adsorption, as well as a decrease in the polarizability of ions in the series $Li^+$, $Na^+$, $K^+$, a symbiotic increase in the rate constants of the monolayer filling of the adsorption layer is observed. Under the conditions of the formed surface layer, lignosulfonates change the sign of the charge to the opposite. Thus, with an increase in the valence of the cation included in the composition of lignosulfonates, their molecular weight and adsorption capacity increase.

## Conclusion

The above allows us to conclude that the technical sulfonates obtained in various modes of delignification differ significantly in composition, structure and, as a consequence, in surface-active properties. Theoretically, the surface activity of lignosulfonates can favorably affect the performance characteristics of paint and varnish materials, but the proof of this requires additional research.

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