

Physicochemical Properties of Lignohumic Acids and Their Salts

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Abstract

Physicochemical properties of lignohumic acids, colloid properties of aqueous solutions of their salts (surface tension, limiting wetting angle, viscosity) have been investigated. Using IR and ESR spectroscopy, the structure of lignohumic acids has been determined. The properties of lignohumic acids have been compared with those peat humic acids. It has been demonstrated that as far as the properties are concerned, the lignohumic acids are close to humic acids of peat.

Key words: hydrolytic lignin, thermolysis, lignohumic acids, humic acids, surface tension, limiting wetting angle

INTRODUCTION

The importance of humic preparations in human economic activities permanently increases due to a set of properties exhibited in the biosphere and, first of all, in the hydrosphere. Firstly, these properties represent a high complex formation ability of humic acids (HA) as naturally occurring polymers-polyelectrolytes; secondly, by their environmental safety and, thirdly, by a lower cost in comparison with synthetic analogues [1].

According to a commonly known concept of the origin of humic substances [2], lignin represents one of the initial substances whose oxidative conversion just resulted in forming all the range of humic compounds in the biosphere. For the purposes of the industrial processing, it is much more efficient to use lignin as a raw material exhibiting more stable properties in comparison with peat, sapropel, coal and other kinds of humic raw.

The present study is devoted to a complex estimation of the structure and colloid-chemical properties of lignohumic acids (LHA) obtained basing on hydrolytic lignin (HL) in the course of its thermochemical modification.

EXPERIMENTAL

As a raw material, we used HL from waste piles of the Bobruysk Hydrolysis Factory. Lignohumic acids were obtained *via* HL thermolysis in the presence of alkali (NaOH) with the subsequent extraction of water-soluble compounds from thermolytic products and the further precipitating LHA in acidic medium [3]. Humic acids were isolated from upper cotton-grass peat with the decomposition level of 45% using the method of reverse alkali extraction [4]. The properties LHA obtained were compared with the properties of HA preparations isolated within the range of pH 3.8–6 (fraction 5 in [4]).

In order to simplify the perception of the material, a sample isolated from peat, we shall designate as peat HA.

In order to study the structure of LHA, peat HA and preparations based on LHA we used the methods of ESR and IR spectroscopy. IR spectra were registered within the wave number range of $4000\text{--}400\text{ cm}^{-1}$ employing an automated complex on the basis of Specord M-80 spectrophotometer and PC [5]. Samples were prepared using a standard technique of pressing pellets with KBr. The content of a substance under investigation in the pellet amounted to 0.35–0.4 %. The registration of ESR spectra was carried out employing a modified RE-1301 ESR spectrometer at a room temperature in an atmosphere of air. The spectra of samples under investigation were registered simultaneously with a reference MgO sample with micro-impurities of Mn^{2+} и Cr^{3+} ions developed at the Institute of Nature Management of the Belarusian Academy of Sciences [6]. This allowed us to improve considerably the accuracy of determining the parameters of ESR spectra as well as to monitor the level of microwave power supplied into the resonator. In order to increase the information value the registration of ESR spectra was carried out at low and high levels of microwave power (0.1 and 50 mW, respectively).

Colloid properties of LHA and their salts were studied using the method of viscosimetry, of surface tension isotherms for aqueous solutions (according to the maximal pressure value in air bubble), the measurements of the

limiting wetting angle for Na–LHA aqueous solutions at the surface of polythene and paraffin plates [7].

The wetting angle was measured via optical method with the help of a horizontal measuring microscope in the following manner. In front of a microscope, a support with a glass plate was installed with a glass plate fixed on it covered with a polyethylene film. Employing a microsyringe, a drop of the aqueous solution of the preparation under study with various concentrations was applied onto this film. For all the experiments the volume of a drop amounted to $2\text{ }\mu\text{L}$. A similar experiment was repeated for a paraffin plate [7], *i. e.* for hydrophobic surface.

RESULTS AND DISCUSSION

As the result of the investigation of the potential exchange capacity for LHA and peat HA, we have established that NaOH titration curves for peat HA and LHA are almost coinciding (Fig. 1). Somewhat divergence between them within the range of pH 5–7 indicates that the peat HA, to all appearance, contains more carboxylic groups as compared to LHA. The discontinuity on the titration curve within the range of pH 7–8 could be connected with buffer properties of LHA, *i. e.* within this range the majority of functional groups is titrated, whereas the alkali introduced (OH^-) is almost no consumed for the neutralization of LHA acid groups. According to the data from [8], within the range of values pH 7–8 the dissociation is

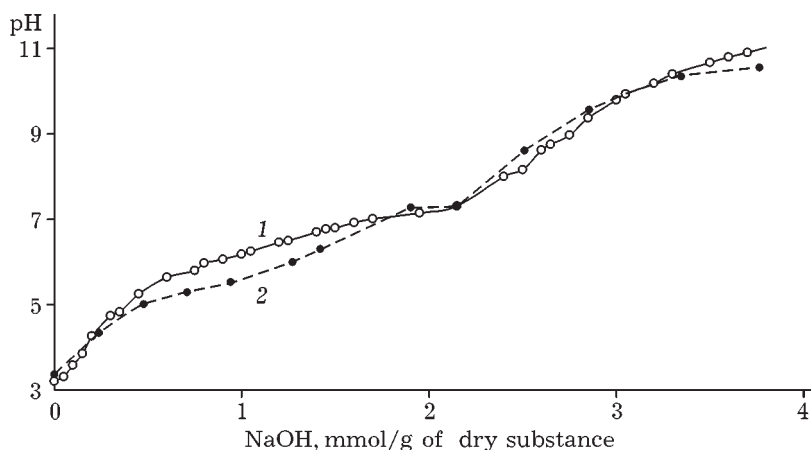


Fig. 1. Titration curves for LHA (1) and peat HA (2) with NaOH. The concentration of LHA and HA in the solution is equal to 0.15 mass %.

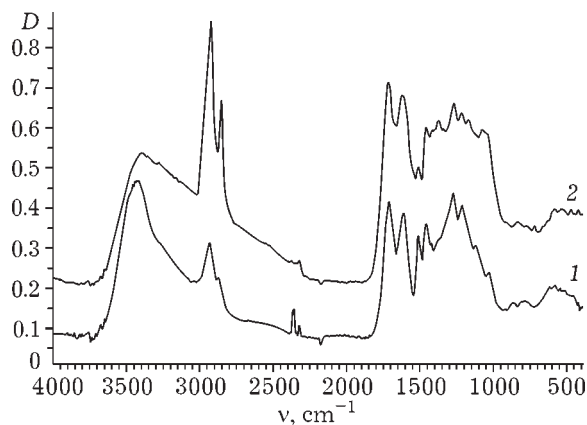


Fig. 2. IR spectra of LHA (1) and HA (2).

inherent in functional groups at aliphatic chains (first of all carboxylic groups).

The comparative analysis of HA and LHA IR spectra supports the opinion concerning the presence of similar functional groups in the structure (Fig. 2).

The following absorption bands of the IR spectrum are inherent in LHA: 3450 cm^{-1} , m. b. – the valence vibrations of hydroxyl OH groups; $2960\text{--}2850\text{ cm}^{-1}$, m. – the valence vibrations of CH_2 and CH_3 groups; $1720\text{--}1700\text{ cm}^{-1}$, s. – the valence vibrations of $\text{C}=\text{O}$ in carboxylic groups; 1610 cm^{-1} , s. – the valence vibrations of conjugated $\text{C}=\text{C}$ groups in polyaromatic structures; 1515 cm^{-1} , s. – the valence vibrations of $\text{C}=\text{C}$ groups in the monoaromatic ring; 1460 cm^{-1} , m. – skeletal vibration of the benzene rings and asymmetric deformation vibrations of CH_3 group; $1270, 1215\text{ cm}^{-1}$, m. – the deformation vibrations of phenolic OH groups and the valence vibrations of $\text{C}-\text{O}$ fragment in guaiacyl aromatic structures [9, 10].

According to the general view (the position of maxima of bands) the IR spectra of LHA and HA are similar to each other. However, there are differences in the ratio between the intensities of LHA bands: the absorption bands of CH_2 groups at 2920 and 2850 cm^{-1} are considerably less abundant than for HA. Correspondingly, the bands of CH_3 groups at 2960 and 2870 cm^{-1} are more clearly exhibited, which indicates the absence of long-chain hydrocarbons in the structure of LHA. And on the contrary, more intense bands at $1515, 1460, 1270$ and 1215 cm^{-1} in LHA spectrum confirm that they are enriched with aromatic structures.

The parameters of the ESR spectrum (Table 1) for LHA are close to those for peat HA: the complete coincidence of g -factor values, profound saturation of the signal with microwave power (a low value of A/A_0 parameter) as well as appearing an additional wider spectrum at a high level of microwave power. At the same time, a much higher signal width is inherent in the spectrum of LHA, which could be observed for HA from lowland kinds of peat owing to the contribution of superfine interaction of unpaired electron with the magnetic nucleus of nitrogen [11]. It is reasonable that in the case of LHA the influence of nitrogen atoms is impossible, which is indicated by a low value of A/A_0 parameter (see Table 1). In order to explain this phenomenon one should take into account the fact that the paramagnetism of HA is caused mainly by “plane” systems of polyconjugation [12]. Owing to a higher content of aromatic rings in the structure of lignin it is quite reasonable to expect that the size of its polyconjugated fragments is

TABLE 1

Parameters of ESR spectra for the samples under investigation

Samples	$\Delta H_{0.1\text{ mW}}$, Gs	$\Delta H_{50\text{ mW}}$, Gs	$g_{0.1\text{ mW}}$	$g_{50\text{ mW}}$	$I, 10^{17}\text{ g}^{-1}$	A/A_0
HL	5.1	4.9	2.0035	2.0036	2.8	2.35
HL thermolyzed	7.5	8.0	2.0046	2.0048	187	4.75
LHA (H-form)	5.3	6.0	2.0036	2.0038	9.9	1.73
High-moor peat HA (H-form)	4.4	4.4	2.0036	2.0038	74	1.90

Note. $\Delta H_{0.1\text{ mW}}$, $\Delta H_{50\text{ mW}}$ are the values of ESR spectrum width at the microwave power amounting to 0.1 and 50 mW, respectively; $g_{0.1\text{ mW}}$, $g_{50\text{ mW}}$ are the values of g -factor at the microwave power amounting to 0.1 and 50 mW, respectively; I is the concentration of the paramagnetic centers; A/A_0 is the ratio between the values of signal amplitude registered at 50 and 0.1 mW.

greater than for HA. This, in turn, results in amplifying the anisotropy, which g -factor mainly determines the signal width for polyconjugated aromatic systems. This is in a good agreement with a higher concentration of paramagnetic centres (PMC) in LHA.

The data presented indicate that according to their structure of the LHA polyconjugation systems are close to those inherent in high-moor peat HA, though they differ in considerably large size of polyconjugation systems.

The values of the g -factor for the ESR signal of the initial HL sample are lower as compared to those for lignin preparations (2.0044–2.0045 [11], which could be explained by the destruction of ethereal bridges between aromatic rings. The present fact indicates the humifying processes to proceed in the course of storing HL in waste piles, *i.e.* its oxidative transformation.

As it follows from data presented in Table 1, the thermochemical processing of lignine results in an almost two order of magnitude increase in the concentration of PMC, with a considerable spectrum broadening, and with an increase in its g -factor. It should be noted that thermal processing of an organic substance results, as a rule, in decreasing the g -factor owing to the destruction oxygen-containing fragments [13]. In our case one should take into account the presence of NaOH therefore the width of the g -factor for thermally treated lignin completely coincides with established values for semiquinone (SQ) radical anions [14]. The treatment of HA preparations and their model analogues by alkaline aqueous solution at a room temperature also results in the generation of high SQ radical concentration. The parameters of their ESR signal differ to a considerable extent from the spectrum of the initial preparation, which could be caused by the presence of polyconjugated aromatic systems. The decrease of the PMC signal relaxation time as compared to the initial sample of lignin (increase in the A/A_0 parameter) also indicates that there SQ radicals formed [15, 16]. The results obtained indicate the basic feature of thermolysis in the presence of alkali, which provides the preservation of functional groups.

The features of the ESR spectrum of HA sample under investigation such as narrow peak of the signal, profound saturation with micro-

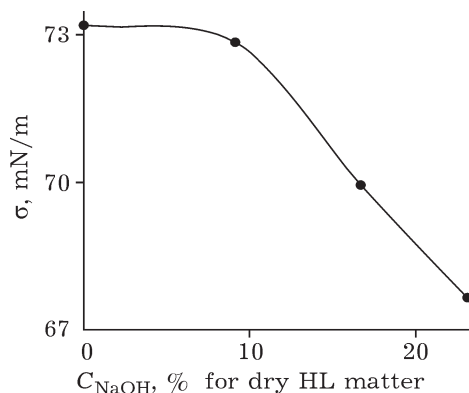


Fig. 3. Change of a surface tension of aqueous solutions ($C_{\text{LHA}} = 2.5 \%$) Na-LHA under various conditions of thermochemical modification lignin.

wave power (low A/A_0 value) with the occurrence of an additional wider spectrum ($\Delta H \sim 15 \text{Gs}$) at a high level of microwave power are typical for HA of high-moor peat and their model analogues those do not contain polyconjugated nitrogen atoms in the systems [11].

In studying the colloid chemical properties LHA sodium salts (Na-LHA) it has been established that Na-LHA aqueous solutions exhibit a lower surface tension as compared to Na-HA (Fig. 3) [17]. This fact indicates the prevalence of non-polar fragments in the molecular structure of LHA those provide high superficial activity for LHA salts.

The comparative analysis of data presented in Figs. 2 and 4 (the absorption intensity within the wave number range for aliphatic and aromatic fragments of LHA and HA) demonstrates that the prevalence of hydrophilic fragments (ionized functional groups) does not result in the decrease of the surface tension for

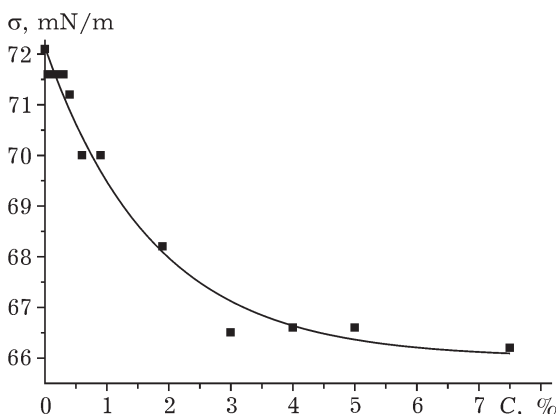


Fig. 4. Surface tension (σ) for aqueous Na-LHA solutions depending on Na-LHA concentration.

aqueous solutions of these compounds. On the contrary, in case that there are non-polar fragments present in the molecular structure they are rejected from the bulk of polar solvent (water) towards the liquid-gas interface, which is neatly accompanied by a decrease of the solution surface tension. However, the ratio between the amount of polar and non-polar fragments in the molecular structure should be balanced, otherwise the compound dissolved would be located within one of the phases, that is why it could not change free (surface) energy at the interface of the phases (the surface tension of the solution). Basing on this fact the hydrophilic balance between the molecular associates of Na-LHA is shifted towards the phobic condition, to all appearance, due to a lower density of polar groups in the structure of LHA comparing to peat HA. This fact could be caused by the method of Na-LHA isolation and initial raw material (lignin) transformation.

As it follows from data presented in Fig. 4, Na-LHA exhibit well pronounced surface active properties, reducing in particular the surface tension of solutions at the liquid-gas interface down to 66 mN/m. The critical concentration of micelle formation (CCM) for Na-LHA corresponds to the concentration in the solution equal to 3 mass %, *i.e.* exceeding this value is not accompanied by the further decrease in the σ of the solution (see Fig. 4).

The wetting of the surface of solids in practice is usually estimated by the contact angle α between the surface of the solid and the tangent with respect to the liquid surface from any point of the

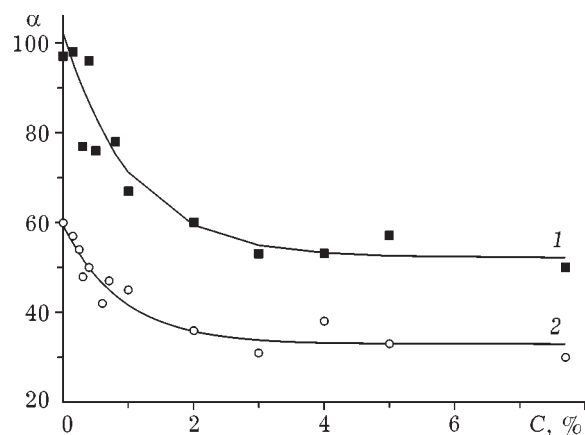


Fig. 5. Variation in the limiting wetting angle (α) for paraffin (1) and polyethylene (2) substrate depending on the concentration of aqueous Na-LHA solution.

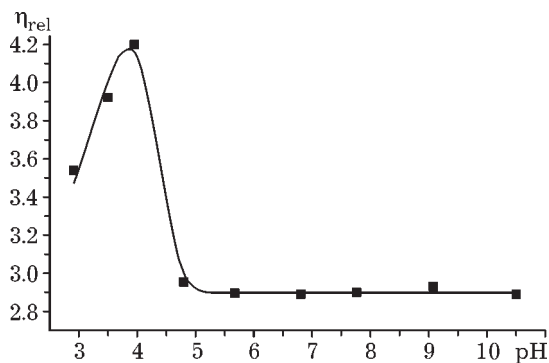


Fig. 6. Variation in the relative viscosity (η_{rel}) of an aqueous LHA solution depending on the medium pH ($C_{LHA} = 5$ g/L).

perimeter of wetting [8]. The contact angle or the wetting angle is counted from the liquid side.

As it follows from the data obtained (Fig. 5), aqueous solutions of Na-LHA promote the reduction of the limiting wetting angle of polythene, paraffin, *i.e.* reduce the surface tension at the solid-liquid interface.

The viscosity properties of Na-LHA aqueous solutions obey the same law as Na-peat HA aqueous solutions. The dependence of changing the relative solution viscosity (η_{rel}) on the medium pH could be symbolically divided into three stages, with an extremum at $pH \approx 4$ (Fig. 6).

The first stage consists in increasing the viscosity at pH 2-4 (the stage of aggregation). The viscosity increase is connected with LHA aggregation owing to the reduction of the surface charge of colloidal structures with the maximum in the region of isoelectric LHA state. The second stage is characterized by decreasing the viscosity at pH 4-5 (the stage of disaggregation). At the given stage, the LHA aggregates are inclined to disintegration owing to coulomb repulsion. The third stage is characterized by constant Na-LHA viscosity at $pH \geq 5$ (the stage of aggregation stability due to the forces of coulomb interaction). The viscosity change could be caused either by changing the surface charge density of high-molecular LHA compounds or by the further change in the second order structure.

CONCLUSION

Basing on the aforementioned results of the studies one could draw the following conclusions:

1. The surface tension of Na–LHA solutions is much lower as compared to that for Na–HA, which indicates the prevalence of non-polar fragments providing high superficial activity of LHA salt forms in LHA molecular structure.

2. Using the method of potentiometry, it has been demonstrated that the products of thermochemical lignin modification represent the compounds of acidic nature similar to peat HA.

3. The analysis of IR spectra obtained for HA and LHA, and also the data [18] allows one to draw a conclusion concerning the prevalence in last aromatic phenol-like structures.

4. The presence of alkali in the thermolysis of HL promotes the conservation of its functional groups in the products of thermolysis (LHA).

5. ESR spectra indicate the similarity of polyconjugation systems for LHA and peat HA, with a greater their content in the structure of LHA.

6. LHA differ from classical HA (isolated from peat) in a big sizes of “plane” polyconjugation systems, which explains their well-pronounce coagulation thresholds.

Thus, the use of HL for obtaining LHA results in forming the products close to peat HA in some physicochemical properties. Owing to the presence of functional groups in the structure of LHA (carboxyl, hydroxyl, *etc.*), the LHA could be used as ion-exchange materials, as well as the basic component for developing the sorbents of heavy metal ions, and other preparations for nature protection purposes.

REFERENCES

- 1 A. M. Abramets, I. I. Lishtvan, N. V. Churaev, II Mezhdunar. Konf. “Guminovye Veshchestva v Biosfere” (Proceedings), Moscow, 2004, p. 145.
- 2 D. S. Orlov, *Gumusovye Kisloty Pochvy i Obshchaya Teoriya Gumifikatsii*, Izd-vo MGU, Moscow, 1990.
- 3 E. V. Kachanov, *Vestsi NAN Belarusi. Ser. Biyal. Navuk*, 5 (2005) 103.
- 4 I. I. Lishtvan, F. N. Kaputskiy, Yu. G. Yanuta *et al.*, *Khim. Tv. Topl.*, 4 (2006) 3.
- 5 Yu. Yu. Navosha, III Vseros. Konf. “Guminovye Veshchestva v Biosfere” (Thesises), St. Petersburg, 2005.
- 6 Inventor’s Certificate No. 1228001 USSR, 1986.
- 7 V. I. Baranova, E. E. Bibik, N. M. Kozhevnikova *et al.*, *Praktikum po Kolloidnoy Khimii*, in I. S. Lavrov (Ed.), *Vysshaya Shkola*, Moscow, 1983.
- 8 G. F. Zakis, *Funktsionalny Analiz Ligninov i Ikh Proizvodnykh*, Zinatne, Riga, 1987.
- 9 K. Nakanisi, *Infrared Spectra and Structure of Organic Compounds* [Russian Translation], Mir, Moscow, 1965.
- 10 K. V. Sarkanen, K. Kh. Ludvig (Eds.), *Ligniny*, Lesn. Prom., Moscow, 1975.
- 11 I. I. Lishtvan *et al.*, *Vestsi AN BSSR. Ser. Khim. Navuk*, 4 (1990) 7.
- 12 V. M. Dudarchik, S. G. Prokhorov, T. P. Smychnik, V. P. Strigutskii, L. V. Strigutskii, *Dokl. NAN Belarusi*, 47 (2003) 78.
- 13 N. A. Bach, A. V. Vannikov, A. D. Grishina, *Elektroprovodnost i Paramagnetizm Polimernykh Poluprovodnikov*, Nauka, Moscow, 1971.
- 14 B. S. Prabhananda, *J. Chem Phys.*, 79, 12 (1983) 5752.
- 15 B. I. Liogonkiy, V. P. Strigutskiy, R. Z. Aleksan, *Dokl. AN BSSR*, 25, 9 (1981) 825.
- 16 Yu. Yu. Navosha, V. P. Strigutskiy, B. I. Liogonkiy, *Khim. Tv. Topl.*, 2 (1982) 24.
- 17 I. I. Lishtvan, II Mezhdunar. Konf. “Guminovye Veshchestva v Biosfere” (Proceedings), Moscow, 2004, p. 96.
- 18 Yu. G. Yanuta, *Polucheniye i Regulirovaniye Svoystv Sorbtionnykh Materialov na Osnove Guminovykh Veshchestv Torfa* (Author’s Abstract of Candidate’s Dissertation in Technical Sciences), Minsk, 2006.