**Full Paper** 

Reference Object Identifier – ROI: jbc-02/17-49-1-84 Subsection: Physical Chemistry. Publication is available for discussion in the framework of the on-line Internet conference "Butlerov readings". http://butlerov.com/readings/ Submitted on January 31, 2017.

Characteristic of polymer properties and structure of Pepper's lignin macromolecules in dimethylformamide

© Anatoly P. Karmanov, <sup>1,3\*+</sup> and Ludmila S. Kocheva<sup>2</sup>

<sup>1</sup>Biochemistry and Biotechnology Laboratory. Institute of Biology, Komi Scientific Center, Ural Division, Russian Academy of Sciences. Kommunisticheskaya St., 28. Syktyvkar, 167982. Komi Republik. Russia. Phone: +7 (909) 120-81-63. E-mail: apk0948@ib.komisc.ru

<sup>2</sup> Chemistry Mineral Raw Material Laboratory. Institute of Geology, Komi Scientific Center, Ural Division,

Russian Academy of Sciences. Pervomajskaja St., 54. Syktyvkar, 167982. Komi Republik. Russia.

Phone: +7 (8212) 24-54-16. E-mail: lskocheva@geo.komisc.ru

<sup>3</sup> The Department of General and Applied Ecology. Department of Thermal Engineering and Hydraulics.

Syktyvkar Forest Institute (Branch) of the Saint-Petersburg State Forest Technical University Named after

S.M. Kirov. Lenina St., 39. Syktyvkar, 167982. Komi Republik. Russia.

Phone: +7 (909) 120-81-63. E-mail: apk0948@ib.komisc.ru

\*Supervising author; <sup>+</sup>Corresponding author

*Keywords:* lignin, hydrodynamic properties, topology of macromolecules, scaling.

## Abstract

An experimental study of hydrodynamic properties and topological structure of the macromolecules of Pepper's lignine, isolated from aspen wood *Populus tremula*, is carried out. The element composition of the lignin's preparation being is: C 58.6%; N 5.5%; O 35.9%. The gross-formula of the monomer unit being is C<sub>9</sub>H<sub>104</sub>O<sub>31</sub>(OCH<sub>3</sub>)<sub>160</sub>. For determining the transport characteristics of macromolecules in the system "lignindimethylformamide" the methods of capillary viscosimetry, translational isothermal diffusion and high-speed sedimentation were used. For calculation of the intrinsic viscosity  $[\eta]$  of the investigated polymer fractions the Huggins equation was applied. It is shown that the values  $[\eta]$  of fractions are located in the interval 3.1-12.2 of sm<sup>3</sup>/g when the molecular weight of the fractions  $M_{SD}$  being is (7.3-30.8)·10<sup>3</sup>. Molecular weight  $M_{SD}$  was determined by Svedberg's method on the basis of the experimental values of the high-speed sedimentation coefficient S, diffusion coefficient D and Archimedes buoyancy factor of the system "lignin-dimethylformamide". The coefficients of sedimentation S vary in the values range 1.3-3.15 Sv, while the diffusion coefficients D vary in the interval  $(7.1-24.7) \cdot 10^{-7}$  sm<sup>2</sup>/s. On the basis the analysis of the lignin's hydrodynamic characteristics the scaling and conformational parameters of macromolecules, and also hydrodynamic Tsvetkov-Klenin invariant A0 were determined. The average value of this parameter for the investigated lignin being is  $A_0 = 2.8 \cdot 10^{-10} \text{ erg/deg mol}^{1/3}$ , which is substantially lower than the theoretical and experimental values for the typical linear macromolecules. It is determined that depending on the value of molecular weight (number of fraction) the value of the Huggins coefficient k<sub>H</sub> is located in the interval 0.32-1.2. The analysis of hydrodynamic data made it possible to conclude about the satisfiability of the principle of scale invariance (scaling). The investigated polymer is characterized by the following Mark-Kuhn-Houvink equations:  $[\eta] = 2.9 \cdot 10^{-4} \cdot M^{0.59}$ ,  $S = 5.2 \cdot 10^{-16} \cdot M^{0.63}$ , D =1.6.10<sup>-4</sup>·M<sup>0.53</sup>. Obtained data show that the aspen lignine relates to the class of the branched polymers. This is confirmed by the low values of intrinsic viscosity  $[\eta]$ , with the lowered value of hydrodynamic Tsvetkov-Klenin invariant A<sub>0</sub> and with the high values of the Huggins coefficient k<sub>H</sub>. The set of the hydrodynamic, conformational and scaling parameters testifies about the star-like topological structure of the aspen lignine.

## References

[1] K.G. Bogolitsyn, V.V. Lunin et al. Physical chemistry of lignin. M.: Akademkniga. 2010. 489p. (russian)

- [2] J.M. Pepper, P.E. Baylis, E. Adler. The isolation and properties of lignin obtained by the acidolysis of spruce and aspen woods in dioxane-water. Canad. J. Chem. 1959. Vol.37. No.8. P.1241-1245.
- [3] P.P. Nefedov, P.N. Lavrenko. Transport methods in analytical chemistry of polymers. L.: Chemistry. **1979**. 232p. (russian)
- [4] I.I. Tverdokhlebova. Conformation of macromolecules. M.: Chemistry. 1981. 284p. (russian)
- [5] V.P. Budtov. Physical chemistry of polymer solutions. SPb.: Chemistry. 1992. 384p. (russian)

- [6] V.N. Tsvetkov, V.E. Eskin, S.Y. Frenkel. Structure of macromolecules in solutions. Moscow: Nauka. **1964**. 720p. (russian)
- [7] V.N. Tsvetkov. Rigid-chain polymer molecules. Leningrad: Nauka. 1986. 380p. (russian)
- [8] V.N. Tsvetkov, P.N. Lavrenko, S.V. Bushin. Hydrodynamic invariant of polymeric molecules. Successes of Chemistry. 1982. Vol.51. No.10. P.1698-1732. (russian)
- [9] G.M. Pavlov, E.V. Korneeva, E.V. Vikhoreva, S.E. Harding. Hydrodynamic and molecular characteristics carboxymethylchitin in solution. Polymer Science. Ser. A. 1998. Vol.40. No.12. P.2048-2055. (russian)
- [10] G.M. Pavlov, E.V. Korneeva, S.A. Nepogodiev, K. Jumel, S.E. Harding. Translational and rotational friction of the molecules of lactodendrimers in solutions. Polymer Science. Ser. A. 1998. Vol.40. No.12. P.2056-2064. (russian)
- [11] A.P. Karmanov, A.G. Dontsov. Investigation of linear and star-shaped macromolecules of lignin. Butlerov Communications. 2015. Vol.43. No.8. P.47-51. ROI: jbc-02/15-43-8-47
- [12] A.P. Karmanov, Yu.B. Monakov. Hydrodynamic properties and structure of lignin. Intern. J. Polymeric. Mater. 2000. Vol.48. P.151-175.
- [13] A.P. Karmanov, M.S. Polemikos, L.S. Kocheva. Theoretical and experimental modeling of lignin biosynthesis. Butlerov Communications. 2015. Vol.41. No.3. P.147-151. ROI: jbc-02/15-41-3-147
- [14] G.V. Kozlov, K.B. Temiraev, V.A. Sozaev. Estimation of fractal dimensions of macromolecular coil in a dilute solution viscosity characteristics. Journal of Physical Chemistry. 1999. Vol.73. No.4. P.766-768. (russian)
- [15] A.P. Karmanov, D.V. Kuz'min, I.N. Shamshina, V.Y. Belyaev, L.S. Kocheva, D.V. Matveev, Y.B. Monakov. Study of hydrodynamic and conformational properties of ligning from woody plants Sorbus aucuparia and Robinia pseudoacacia. Polymer Science. Ser. A. 2004. Vol.46. No.6. P.997-1004. (russian)