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

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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 $C_9H_{10.4}O_{3.1}(OCH_3)_{1.60}$. For determining the transport characteristics of macromolecules in the system "lignin–dimethylformamide" the methods of capillary viscosimetry, translational isothermal diffusion and high-speed sedimentation were used. For calculation of the intrinsic viscosity [η] of the investigated polymer fractions fhe Huggins equation was applied. It is shown that the values [η] of fractions are located in the interval 3.1-12.2 of sm^3/g when the molecular weight of the fractions M_{SD} being is $(7.3\text{-}30.8)\cdot10^3$. 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 $(7.1\text{-}24.7)\cdot10^{-7}$ sm^2/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 A_0 were determined. The average value of this parameter for the investigated lignin being is $A_0 = 2.8\cdot10^{-10}$ 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_H 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: $[\eta] = 2.9\cdot10^{-4}\cdot M^{0.59}$, $S = 5.2\cdot10^{-16}\cdot M^{0.63}$, $D = 1.6\cdot10^{-4}\cdot M^{0.53}$. 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 [η], with the lowered value of hydrodynamic Tsvetkov-Klenin invariant A_0 and with the high values of the Huggins coefficient k_H. 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. *Moscow: 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. *Moscow: Chemistry.* **1981**. 284p. (russian)
[5] V.P. Budtov. Physical chemistry of polymer solutions. *St. Petersburg.: 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. DOI: 10.37952/ROI-jbc-01/15-43-8-47
[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. DOI: 10.37952/ROI-jbc-01/15-41-3-147
[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 lignins from woody plants Sorbus aucuparia and Robinia pseudoacacia. *Polymer Science. Ser. A.* **2004**. Vol.46. No.6. P.997-1004. (russian)