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DENSITIES OF DEHYDROGENATED POLYMER SOLUTIONS IN DIMETHYLSULFOXIDE

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Densities of dehydrogenated polymer (DHP) solutions in DMSO have been investigated in the temperature range 20–70°*C*. It has been shown that the density of the solution with a certain concentration of DHP in DMSO increases progressively with time tending to a constant value, whereas in the case of diluting the density of the solution varies, passing through the maximum point.

Keywords: lignin, dehydrogenated polymer, solution density, structural changes, dimethylsulfoxide.

Introduction. During the last fifthen years the study of the structure and composition of vegetal cell wall has obtained a very high expansion. The interest in the field of cell wall systems is relied, on the one hand, on the limited quantity of fossil energetical resources on the heart and, on the other hand, on the objective to prepar new biodegradable materials. Great attention is paid to replace synthetic polymers by natural renewed materials, which, in occurence of synthetic polymers, are ecologically non dangeruses for environnement. For this purpose, the plant cell wall is a very important source of natural polymer compounds and of renewable carbon (cellulose, lignin, etc) [1, 2].

Lignocellulosic cell wall is a complex and highly complex network of nano or micro sized building blocks, where cellulose micro fibrils are surrounded by hemicelluloses, lignin and proteins. Notably, lignin which is a typical component of lignocelluloses and is involved in a complex phenolic polymer composed of three phenyl propane monomeric building units [3, 4]. Lignin is one of the most abundant natural polymers. Tens of million tons of dissolved lignin are annually produced in the craft pulping process. Owing to its aromatic structure and fewer hydroxyl groups, lignin is generally considered as a hydrophobic polymer. Lignin being intimately associated with polysaccharides in the cell wall is hardly isolated in the native form [5, 6]. Interactions between lignin and polysaccharides in plant cell walls have been extensively studied to improve biomass delignification, which is a key technology for pulp and paper industry. Such interactions are classified into non covalent and covalent bonds, and are responsible for the formation of a dense and highly organized network [7, 8].

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The plant polymer lignin consists of various types of substructures covalently bonded into branched, disordered, polymeric network assemblies [9] (Fig. 1).

The disorder is both chemical, with many different types of substructures and conformational, that is, there is a distribution of relative orientations and separation distances between substructures. Thus, the physicochemical properties (electronic properties for instance) of lignin are considerably more difficult to predict from structure compared to those of artificial polymers, which usually contain only a single type of substructure.

It is well known that the lowest excited electronic singlet states of lignin are responsible for optical (UV-vis) absorption and fluorescence emission properties [9]. Description of electronic states of lignin must take the properties of the individual substructure, which consists of a minimum sized fraction of the lignin polymer, that is, a C_9 lignin monomer unit or, if a path of conjugation exists between two monomers, a lignin dimer unit (such as a stilbene-type unit).

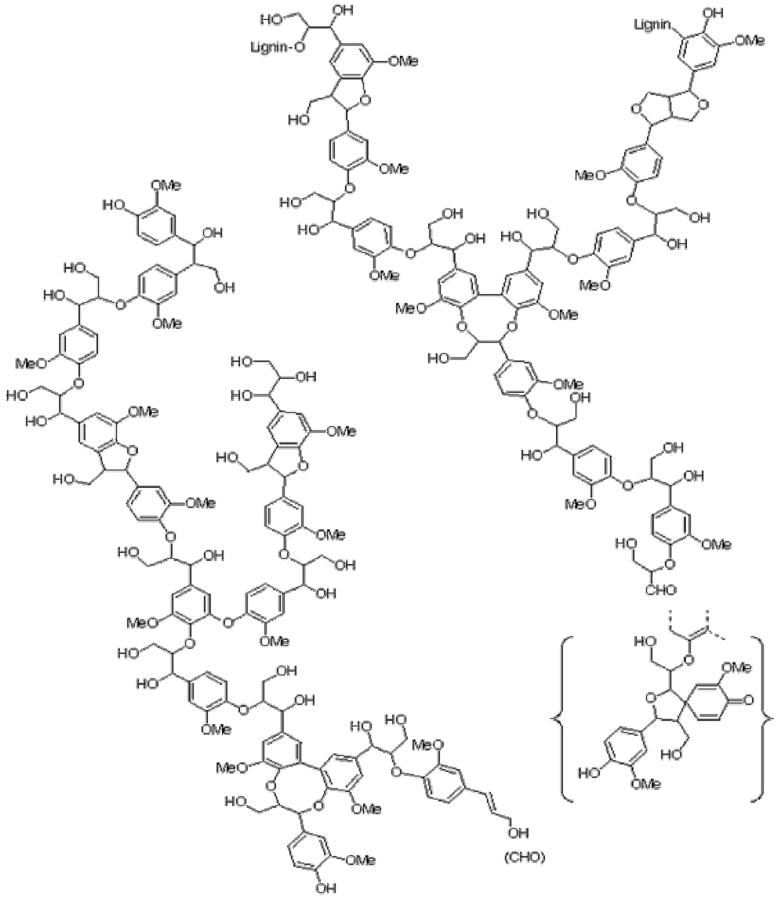

Fig. 1. Tentative structure of lignin, where typical substructure parts are indicated.

This approach of relating optical properties with structural properties is based on the idea that the lignin polymer is a collection of *weakly* interacting chromospheres (in a uniform dielectric medium) analogous to a dilute solution of a limited number of different types of chromospheres, where the term "chromosphere" denotes a set of electronic states with well-defined properties. Thus, each type of chromosphere corresponds to a definite type of chemical substructure [9]. It can be expected that any process, which changes the relative orientations and separation distances between substructures, will modify the electronic properties of lignin. Lignin model components (Dehydrogenation Polymers, DHPs) can also be synthetized by *in vitro* polymerization of lignin precursors using peroxidase/H_2O_2 as oxidizing agent [10].

In our previous works we have shown that during the dilution of DHP solution in small quantity of DMSO the optical (UV-vis) absorption and fluorescence emission properties where dramatically changed [11]. We have explained this phenomenon by opening of DHP molecules during the dilution in DMSO as the results of interactions between polymer and solvent molecules (hydrogen bonds formation between hydroxyl groups of DHP and S=O groups of DMSO, for instance).

In the present article we have studied the changes of densities of DHP solutions during its dilution in small quantity of DMSO and the changes of densities of DHP solutions during the time. The impact of the temperature on the densities of DHP solutions in DMSO was also studied.

Materials and Methods.

Lignin Compounds. Lignin model compound (DHP) was synthesized according to the classical "Zutropfverbaten" method consisting of a slow and continuous addition of coniferyl alcohol (4-hydroxy-3-methoxy-cinnamyl alcohol) and hydrogen peroxide to the solution of peroxidase according to the procedure detailed in [10]. DHP was collected at the end of the reaction by centrifugation of the suspension and the insoluble part was washed with water before freeze-drying. DMSO was purchased from "Sigma Chemical Co" USA (DHP was collected at the end of the reaction by centrifugation of the suspension and the insoluble part was washed with water before freeze-drying). The average weight of molecular mass (M_w) is 2775 $g{\cdot}mol^{-1}$ with a polydispersity index M_w/M_n of 1.4, determined by high-performance size exclusion chromatography using the relative calibration method based on the elution of ten polystyrene standards [10].

The densities of DHP solutions DMSO were measured on an Anton Paar DMA 4500 vibrating-tube densimeter at the temperature range 20–70°*C*. The accuracy of the density and temperature measurements was $\pm 1\times 10^{-5}$ $g{\cdot}cm^{-3}$ and ±0.01 *K*, respectively. The densimeter was calibrated with dry air and doubly-distilled water.

Results and Discussions. In order to check the effect of dilution on the densities of DHP solutions in DMSO the densities of these solutions after successive dilutions were measured. The measurements are carried out at temperature ranges 20–70°*C* (see Table).

From the results presented in Table, it can be seen well that at any concentration of DHP the density of solution linearly decreases when the temperature increases. This observation is in good agreement with the well known behavior of solute systems. On the other hand, whatever the temperature between 20–70°*C* during the successive dilution of solution 0.36 *mol*/*mL* DHP in DMSO is the density first increases and then decreases up to density values of pure solvent (DMSO) (see Table).

The values of DHP solutions density during the dilution in DMSO at the temperature range 20–70°C

DHP, *mol/mL*	Density, *g/cm*^{3}					
	20°*C*	30°*C*	40°*C*	50°*C*	60°*C*	70°*C*
0.360	1.10098	1.09102	1.08102	1.07104	1.06103	1.05101
0.346	1.10105	1.09113	1.08117	1.07119	1.06121	1.05119
0.331	1.10112	1.09125	1.08132	1.07124	1.06135	1.05113
0.306	1.10131	1.09145	1.08151	1.07152	1.06156	1.05144
0.288	1.10144	1.09167	1.08172	1.07181	1.06186	1.05187
0.270	1.10161	1.09186	1.08193	1.07198	1.06199	1.05198
0.234	1.10183	1.09204	1.08221	1.07233	1.06234	1.05252
0.216	1.10184	1.09205	1.08221	1.07234	1.06244	1.05251
0.180	1.10175	1.09198	1.08205	1.07219	1.06231	1.05231
0.144	1.10158	1.09179	1.08187	1.07197	1.06204	1.05208
0.090	1.10125	1.09141	1.08147	1.07157	1.06161	1.05162
0.045	1.10104	1.09103	1.08113	1.07114	1.06124	1.05119
0	1.10068	1.09058	1.08074	1.07074	1.06073	1.05069

For example, in Fig. 2 are presented the density variations plots of DHP solutions (0.18 *mol/mL* (plot a) and 0.36 *mol/mL* (plot b)) at 20–70°*C*.

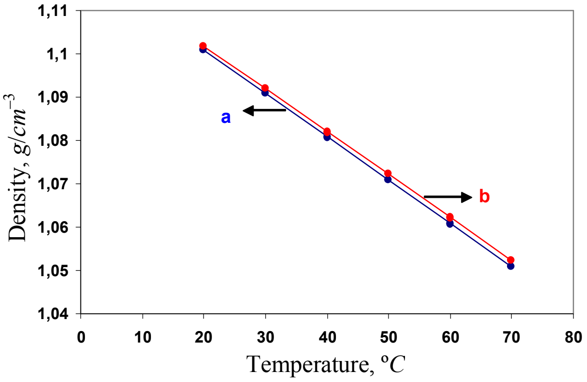

Fig. 2. Density variations plots of DHP solutions in DMSO at 20–70°*C*: a – 0.18 *mol/mL* and b – 0.36 *mol/mL*.

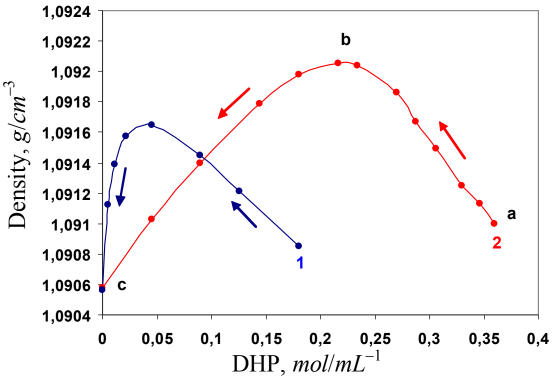

Fig. 3. Plots of the changes of density of DHP solutions (0.18 *mol/mL* (1) and 0.36 *mol/mL* (2)) during the dilution in DMSO at 30°*C*.

As we can see from Fig. 3, for both concentrations the shapes of the density change plots are very similar. During the dilutions of DHP solutions the plots of density change, passing through a maximum point, divide the plots on both ab and bc parts (plot 2). Thus, we can conclude that there are two opposite phenomenon which act differently on the density of solution during dilution.

Increasing of the density (Fig. 3, parte ab) corresponds to the deployment of DHP molecules during the dilution. At the maximum point on the plot (Fig. 3, point b) the DHP molecules are completely deployed in solution. After the maximum point the next dilutions are accompanied by density decrease as an ordinary solution.

It is interesting to note that the density of DHP solution in DMSO changes during the time after the preparation. In Fig. 4 the plots of DHP solutions (0.18 *mol*/*mL* (a) and 0.36 *mol*/*mL* (b)) densities changing during the time at 30°*C* are presented. As it can be seen, in both cases during the time the density of DHP solutions increases and progressively tend to equilibrium values (≈1.0920 $g{\cdot}cm^{-3}$ (plot a) and ≈1.0924 *g·cm*¯3 (plot b)).

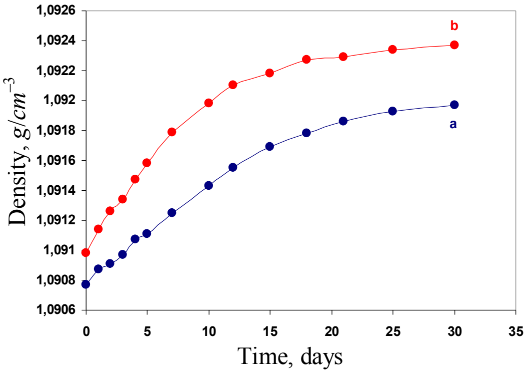

Fig. 4. Plots of the changes of densities of DHP solutions (0.18 *mol*/*mL* (a) and 0. *mol*/*mL* (b), respectively) during the time at 30°*C*.

A probable explanation of observed phenomena is presented in Fig. 5. It can be supposed that in the solution at the DHP–DMSO contact region the structure of DMSO is more compacted than in pure DMSO. In pure DMSO solvent the molecules are relied with each other by hydrogen bonds and form a certain structure, which causes decrease of the densities of solutions.

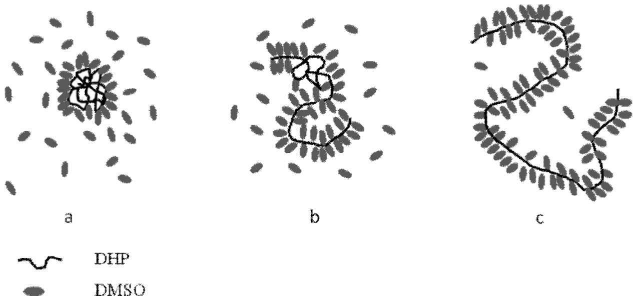

Fig. 5. Different states of deployement of DHP molecule in DMSO.

The introduction of DHP molecules in DMSO is accompanied by rupture of some hydrogen bonds and, consequently, by destruction of inner structure of DMSO. When DHP molecule is in poor solvent condition (the molecules of DHP are compacted) the contact region between DMSO and DHP is smaller (Fig. 5, a) and the density of solution is close to pure DMSO density. During the dilution and/or the time after the preparation of DHP solution DMSO–DHP contact region is increased (Fig. 5, b). Consequently, the density increases progressively up to the maximum value corresponding to complete opening of DHP molecule in solution (Fig. 5, c). After that the density decreases according to the classical solutions dilution mechanism.

Conclusion. The density of DHP solutions in DMSO increases during the time after the preparation of solution and reaches to a constant density value. In the case of dilution of DHP–DMSO solution with small quantity of DMSO the density increases up to a maximum value and after that it decreases up to pure DMSO density value. This phenomenon can be explained by structuration of DMSO molecules in the DHP–DMSO contact region, the area of which is maximal when the DHP molecule is completely opened and has a deployed form in solution.

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