

IN COMMEMORATION OF ACADEMICIAN V. V. LUNIN:
SELECTED CONTRIBUTIONS FROM HIS STUDENTS AND COLLEAGUES

Structural and Dynamic Characteristics of a Water–Ethanol–2-Methoxy-4-(2-Hydroxypropyl) Phenol Mixture under Subcritical Conditions

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Received September 2, 2020; revised September 2, 2020; accepted September 14, 2020

Abstract—The molecule of 2-methoxy-4-(2-hydroxypropyl) phenol (HPP) is a structural unit of coniferous lignin. The results are presented from molecular dynamics modeling of the structural and dynamic parameters of a three-component mixture water–ethanol–HPP at a temperature of 573 K and a density of 0.737 g/cm³, which corresponds to the subcritical conditions of the fluid state. The radial distribution functions between the centers of mass of HPP molecules and mixed solvent molecules, the number of water and ethanol molecules in the solvation shells, the average numbers and average lifetimes of hydrogen bonds, and the coefficients of the self-diffusion of solvent molecules are calculated. It is shown that HPP molecules form hydrogen bonds with each other, as well as with water and ethanol. Hydrogen bonds between HPP molecules are in this case the ones most stable and long-lived.

Keywords: lignin, propylphenol, methoxy-hydroxypropyl-phenol, water–ethanol solutions, subcritical conditions, solvation shells, lifetimes of hydrogen bonds, average numbers of hydrogen bonds

DOI: 10.1134/S0036024421030079

INTRODUCTION

Lignin is an irregular natural polymer with a strongly branched structure and high molecular weight. The main monomer of lignin is the guaiacyl propyl unit. Lignin in the largest volumes today is obtained as a result of cellulose processing (pulp and paper industry, hydrolysis production). Due to its availability and abundance of active functional groups, lignin is considered an ideal feedstock for the production of numerous valuable materials (e.g., phenolic resins, epoxy resins, adhesives, polyolefins, and binders), including renewable biofuels. Among the fields of science developed under the leadership of Academician V.V. Lunin, the study of natural polymers (particularly lignin) and their transformation under conditions of exposure to high temperatures and pressures emerged over the last decade. We now know that the use of supercritical fluids (sub- and supercritical water/aqueous–organic solutions) is a very promising approach for the depolymerization of lignin and its splitting into small molecules. An increase in the solubility of the aromatic framework of lignin during delignification is in this case achieved by using water–organic mixtures, particularly water–phenol, water–

ethanol, and water–methanol. Ethanol is one of the most environmentally friendly organic co-solvents of water [1].

So far, little information has been obtained on the laws governing the chemical transformation of lignin, since the strong dependence of the molecular structure of lignin on the parameters of state, and the nature and concentration of solvents, makes it difficult to identify them. In addition, performing an experiment under sub- and supercritical conditions prevents the use of structure-sensitive techniques. The above thus elevates the role of computer experiments in searching for patterns of lignin transformation. In this work, we investigated the behavior of a lignin monomer unit molecule in an aqueous ethanol solution under subcritical conditions by means of classical molecular dynamics modeling. The 2-methoxy-4-(2-hydroxypropyl) phenol (HPP) molecule, which is capable of forming a β -O-4 bond with another molecule, was used as our model (Fig. 1). The HPP molecule is one of the main structural units of coniferous lignin. The dissolution of lignin in sub- and supercritical water–ethanol mixtures is accompanied by the destruction of its polymer structure, as a result of

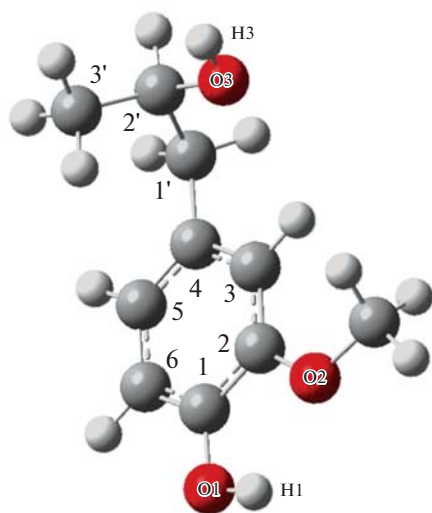


Fig. 1. 2-Methoxy-4-(2-hydroxypropyl) phenol molecule after optimizing its geometry. The numbering of the atoms is shown.

which the monomeric compounds that make it up pass into the solution. The fluid systems studied in this work are thus models of solutions that form as a result of the depolymerization of coniferous lignin in sub- and supercritical water-ethanol mixtures.

The solvation of HPP molecules in water-ethanol solutions of different concentrations (0.020, 0.115, 0.285 mole fractions (ppm) of ethanol) was studied in [2] at a temperature of 573 K and densities corresponding to an experimental pressure of 23 MPa. It was shown that HPP forms hydrogen bonds (HB) with both water and ethanol that are characterized by longer life expectancy than water-water, ethanol-ethanol, or water-ethanol HB. At the same time, water molecules (rather than ethanol) are predominantly surrounded by HPP. Ethanol molecules are included in the solvation shells only around hydroxyl groups O1H1 and O3H3. The total amount of HB in the fluid falls as the concentration of ethanol rises, but their lifespan is extended. In a subcritical fluid medium, solvate complexes formed by HPP with water and ethanol behave as relatively stable structures that exist longer than associates of water and alcohol molecules. An increase in the lifetime of the HB is observed as the concentration of ethanol in the fluid rises (i.e., there is stabilization of solvate complexes and the structuring of solvate shells). An increase in the concentration of ethanol in the fluid does not affect the total number of hydrogen bonds formed by the solute, but it does shorten the lifespan of all hydrogen bonds in the fluid, including the solute-water and solute-ethanol hydrogen bonds. In this work, we investigated the extent to which HPP molecules in an aqueous ethanol medium are able to self-associate under subcritical conditions. We also considered the change in the composition of the solvation shells and the structural and

dynamic characteristics of the fiber upon moving from a model system containing one molecule of a solute to a system containing 8 molecules.

BUILDING A MODEL SYSTEM

The model HPP solute molecule was built on the basis of the structure of 2-methoxy-4-propylphenol [3]. The molecular structure of the HPP was optimized in an approximation of the density functional theory using the B3LYP functional [4, 5] and the 6-31G++ (*d,p*). All calculations were made using the Gaussian 09 software package [6]. The absence of imaginary vibration frequencies confirmed the stationary nature of the resulting structure. The charges on atoms were obtained via NBO analysis. The geometry of the HPP and ethanol molecules and the parameters of interaction were taken from those of the OPLS-AA force field in [7]. Modeling was done using the Gromacs-5.0.7 package [8]. We used a model of a partially non-rigid system in which the geometric parameters of the benzene ring and the methoxy group (O2Me) were fixed for the HPP molecule, rotation relative to the C-O bond was allowed for the hydroxyl group (O1H1), and the bond and torsion angles could be changed for the hydroxypropyl group. For ethanol, we used a completely rigid model of a molecule with parameters from the OPLS-AA force field [7]. Potential TIP4P was used for water molecules.

MOLECULAR DYNAMICS MODELING

Molecular dynamics modeling was done in an NVT ensemble in the full atomic version using the Gromacs 5.0.7 software package [8] with GPU accelerators, which allowed high performance parallel computations to be performed. The Verlet algorithm was used to integrate Newton's equations [9]; a Nose-Hoover thermostat was used to maintain a constant temperature [10, 11]; modified Ewald summation was used to consider long-range electrostatic interactions [12, 13]; and the LINCS algorithm was used to limit all bond lengths [14].

Two systems were modeled: **I** (one HPP molecule) and **II** (eight HPP molecules in a water-ethanol solution (0.02 ppm ethanol) at $T = 573$ K and $\rho = 0.737$ g/cm³. This density corresponds to that of a binary mixture of water-ethanol (0.02 ppm ethanol). Density was calculated by interpolating the experimental data in [15, 16].

A cell was first prepared with a water-ethanol solution that contained 5832 water molecules and 117 ethanol molecules. The binary system was initially equilibrated for 500 ps in a cubic cell with edges of 6.29 nm. The system was heated and thermostatted for 1.5 ns. A cell with edges of 6.3 nm was created for system **I**, into which one HPP molecule was placed and an aqueous ethanol solution was poured. Thermostatting was done for 500 ps at the given values of tempera-

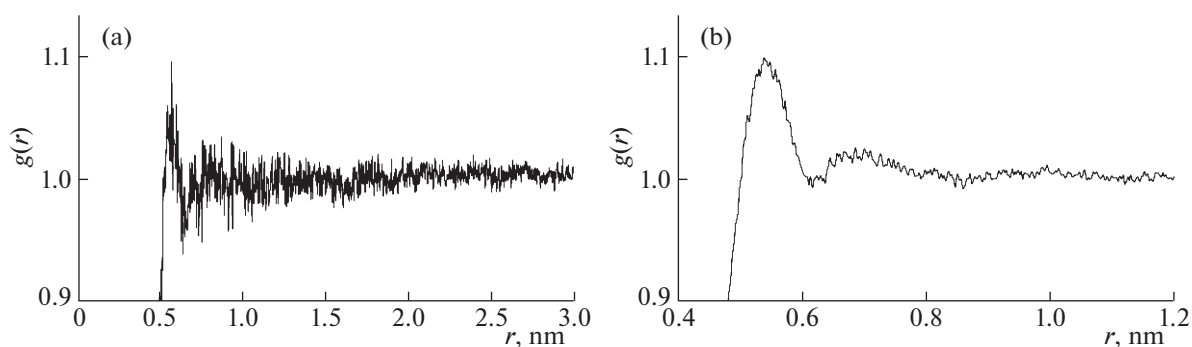


Fig. 2. Radial distribution functions for the centers of mass of HPP molecules and water: (a) system **I**, (b) system **II**.

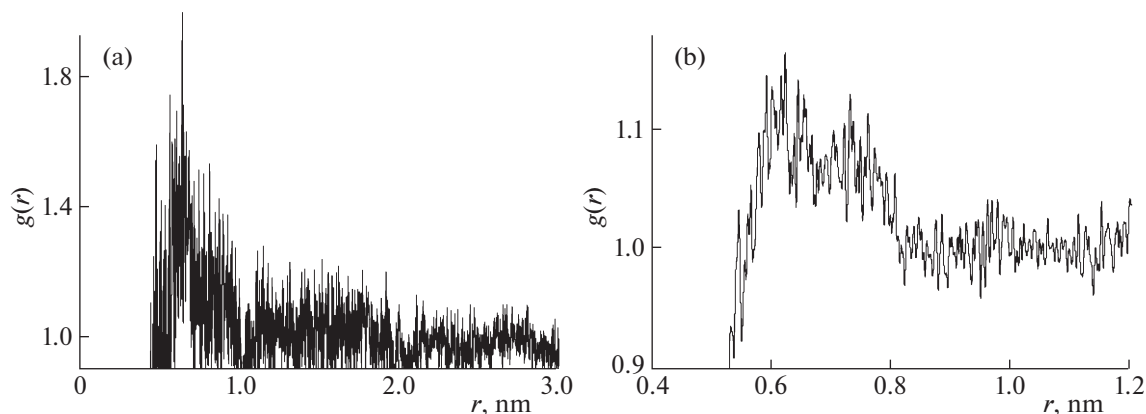


Fig. 3. Radial distribution functions for the centers of mass of HPP and ethanol molecules: (a) system **I**, (b) system **II**.

ture and density. For system **II**, we took the original cell of system **I**, enlarged it by 800%, and compressed it into a cube with edges of 6.31 nm. The cell was then filled with an aqueous ethanol solution, after which the system was thermostatted for 500 ns. The specified size allowed 5832 water molecules, 117 ethanol molecules, and eight HPP molecules to be placed into the cell with a solvent density of 0.737 g/cm³. Fifteen molecular dynamics trajectories were obtained for each system. The periods of data collection for subsequent analysis of static and dynamic properties were 500 ps in 1 fs steps for system **I**, and 1 ns in 0.5 fs steps for system **II**.

RESULTS AND DISCUSSION

Radial distribution functions (RDFs) were calculated for the distances between the centers of mass of the HPP and water molecules (Fig. 2) and between the centers of mass of the HPP and ethanol molecules (Fig. 3). Also calculated were the average numbers of water and ethanol molecules in the solvation shells of different radii (Table 1); the average number and average lifetimes of hydrogen bonds (HB) for molecules of HPP and ethanol (Table 2); the number of hydrogen

bonds formed by individual functional groups of the solute (Table 3); and the coefficients of the self-diffusion of solvent molecules (Table 4).

The RDFs (Figs. 2, 3) show there were solvation shells of water and alcohol molecules around the HPP molecules. The shells were more pronounced in system **I**, where there was only one HPP molecule. The solvation shells of solvent molecules were less pro-

Table 1. Average number N of molecules of water and ethanol in the HPP solvation sphere

N (ethanol)				
Sphere radius, nm	1.0	0.979	0.75	
System I	2.0	1.94	0.8	
System II	1.8	1.7	0.7	
N (water)				
Sphere radius, nm	1.0	0.979	0.75	0.646
System I	91.2	85.5	34.5	19.8
System II	91.7	85.9	35.4	20.4

Table 2. Average numbers n_{HB} of hydrogen bonds with water and ethanol formed by an HPP molecule and individual functional groups of HPPs, and the average lifetimes of the HBs between HPP and water and HPP and ethanol

Parameter	HPP–water		HPP–ethanol	
	System I	System II	System I	System II
n_{HB}	3.75	4.46	0.03	0.05
n_{HB} H1O1	1.09	1.53	0.01	0.03
n_{HB} O2	0.86	1.33	0.01	0.01
n_{HB} H3O3	1.80	1.60	0.01	0.02
τ^{I} , ps	1.06	1.34	0.81	1.82

Table 3. Average number n_{HB} of HBs and average lifetime τ^{I} of HBs between molecules in system II

Type of HB	n_{HB}	τ^{I} , ps
HPP–HPP	0.1	20.84
Water–ethanol	1.44	0.58
Ethanol–ethanol	0.1	0.67

nounced in system II, due apparently to penetrating into the coordination sphere of other HPP molecules. The splitting of the first peak in the RDF for the HPP–ethanol distances in system II is noteworthy. This can be explained by the different functional groups of the HPP molecule being solvated by ethanol molecules in different ways. The smoother form of the RDF for system II relative to system I is due to the high number of HPP molecules that participate in the formation of hydrogen bonds.

By integrating the RDFs from 0 to specific distances (1.000, 0.979, 0.750, and 0.646 nm), the number of solvent molecules in the solvation spheres was obtained at different values of their radii (Table 1). The value of 0.75 nm corresponds to the first minimum on the RDF for HPP–ethanol interactions. The first minimum on the RDF corresponds to a value of 0.646 nm for HPP–water interactions. The number of water molecules in a solvation shell of a fixed size around HPP molecules is slightly larger for system II than in system I, and there are fewer ethanol molecules. This effect can be explained by the displacement of ethanol molecules from the coordination sphere, due to the inclusion of other HPP molecules.

Average numbers n_{HB} of the HBs that formed between the HPP and solvent molecules were analyzed along with their lifetimes. HBs were analyzed for different functional groups of HPP molecules (Table 2). A geometric criterion was used to identify

each HB: the maximum intermolecular distance between oxygen and hydrogen atoms forming a HB was 0.245 nm; between two oxygen atoms, it was 0.360 nm.

Average lifetime $\tau_{\text{HB}}^{\text{I}}$ was calculated to assess the stability of HBs using autocorrelation function (ACF) $C_{\text{Sun}}(t)$ [17]:

$$C_{\text{HB}}(t) = \frac{\langle S_{ij}(0)S_{ij}(t) \rangle}{\langle S_{ij}^2(0) \rangle},$$

where parameter $S_{ij}(t) = 1$ if the HB between molecules i and j formed at the initial moment form at current time t , and the duration of the periods where the criterion was violated in the interval from 0 to t did not exceed predetermined value t^* . Otherwise, $S_{ij}(t) = 0$. When $t^* = \infty$, the result was the ACF of the long-term existence of an HB, $C_{\text{HB}}^{\text{I}}(t)$. Integrating it allowed us to obtain the average lifetime of an HB:

$$\tau_{\text{HB}}^{\text{I}} = \int_0^{\infty} C_{\text{HB}}^{\text{I}}(t) dt.$$

When the HB criterion is violated, the molecules do not always leave each other's coordination sphere. There is a high probability they will approach each other again at the distance specified by the criterion, so lifetime $\tau_{\text{BC}}^{\text{I}}$ gives an accurate idea of the true duration of an HB's existence [18, 19]. We can see from Table 2 that HB's form with the participation of the hydroxy groups H1O1 and H3O3, and to a lesser extent with oxygen atom O2 (methoxy groups). The average numbers of airborne compounds with water around different functional groups are different in system I, but they are the same with ethanol. An HB in this case forms primarily with the participation of hydroxy group H3O3. The average numbers of airborne compounds with water around all functional groups are equal in system II, but they differ with ethanol. Above, we noted the splitting of the first peak into the FRR of HPP–ethanol and indicated this can be explained by the solvation of different functional groups. The lifetimes of the HBs of HPP with ethanol are longer than with water molecules, due probably to the lower mobility of ethanol molecules. The lifetimes are in this case much longer in system II, relative to system I, testifying to the high stability of hydrogen bonds in the system with eight HPP molecules.

The numbers of HBs and the average lifetimes of the components of the fluid were calculated for system II. It was found that due to the larger number of water and ethanol molecules, the greatest number of hydrogen bonds formed between them, while the numbers of ethanol–ethanol and HPP–HPP bonds are relatively low, due to the weak concentration of these molecules. However, the lifetimes of hydrogen bonds between HPP molecules were considerably higher

Table 4. Coefficients of the self-diffusion of water and ethanol molecules: $\Delta D \times 10^5 \text{ cm}^2 \text{ s}^{-1}$

System	Ethanol–water binary system	System I	System II
Ethanol	22.9	22.1	21.7
Water	37.3	37.4	37.6

than those of hydrogen bonds between other components (Table 3). The ethanol–ethanol hydrogen bonds also appear to be more long-lived than those in the water–ethanol system.

Table 4 shows the coefficients of diffusion calculated for solvent molecules. It was found that upon moving from a binary mixture of water–ethanol to a three-component fluid, there is a tendency for the mobility of solvent molecules to grow. We know from the works of Yu.E. Gorbatyi [20, 21] that in the subcritical region, the number of tetrahedrally coordinated water molecules falls when approaching the critical isotherm, testifying to the destruction of the continuous network of water structures. In [2], we showed there are hydrogen bonds between water molecules under subcritical conditions, though their number is reduced relative to normal conditions. With the addition of HPP molecules, there is further destruction of the hydrogen bonds between water molecules and water shells around ethanol molecules, increasing the mobility of water and ethanol molecules. However, this process is inhibited by the formation of longer-lived hydrogen bonds between the HPP molecules and the solvent. This is reflected overall in a slight increase in the coefficient of diffusion of solvent molecules during the formation of a three-component solution. It should be noted that the formation of long-lived HBs between HPP molecules correlates with our earlier data on the formation of long-lived dimers of guaiacol (another model molecule of the monomer lignin unit) under supercritical conditions [22], and experimental data on the formation of products of phenol condensation in supercritical water [23].

CONCLUSIONS

The structural and dynamic parameters of three-component fluids containing HPP molecules in a water–ethanol environment at an ethanol content of 0.02 ppm were studied by means of classical molecular dynamics at a temperature of 573 K and a density corresponding to the experimental pressure of 23 MPa. The numerical parameters characterizing the distribution of components in the solvation shells of the solute were calculated. The numbers and lifetimes of the HBs between components of the fluid were determined. It was shown that HPP molecules form HBs among themselves, and with water and ethanol. The HBs between the HPP molecules are in this case the ones

most stable. Our results have to do with the dynamics of the molecules: heavier components (ethanol and, to a greater extent, HPP) are less mobile and thus form longer-lived HBs. However, the average number of HBs formed between HPP and ethanol or other HPP molecules is very low: in a system with 8 HPP molecules, these are 0.05 and 0.10, respectively, while the average number of HBs with water per HPP molecule is 4.46. We thus conclude that HPP molecules, like the other model molecules of the structural units of lignin (phenol, guaiacol) in a water–ethanol fluid studied earlier, are capable of forming stable hydrogen-bonded associates with one another. However, at specific concentrations chosen such that the solubility threshold of a substance is not exceeded, the formation of such associates is random, and the HPP molecules are uniformly distributed in the volume of the fluid most of the time.

FUNDING

This work was supported by the Russian Foundation for Basic Research, project no. 18-29-06072.

ACKNOWLEDGMENTS

Our calculations were performed on the MVS-100k supercomputer at the Russian Academy of Sciences' Joint Supercomputer Center.

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SPELL: 1. guaiacol