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Specific features of solvation of lignin related phenols in the binary mixtures of water with dimethyl sulfoxide, 1,4-dioxane, and acetonitrile*

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The effect of the solvent composition in the binary mixtures of water with dimethyl sulfoxide, acetonitrile and 1,4-dioxane on the positions of absorption bands in the UV spectra of five guaiacylic phenols, as well as of the corresponding phenolate anions, simulating structural units of natural lignin macromolecules, was studied. The data obtained were interpreted based on the model of a stepwise solvent exchange in the solvation shells. Parameters of a preferential solvation and compositions of solvation shells of lignin related phenols were calculated. A determining role of water complexes with aprotic solvents in the solvation equilibria involving phenols under study was shown.

Key words: lignin, phenols, solvatochromism, mixed solvents, preferential solvation.

In the last years, the interest to the processing of renewable plant materials (biorefining) as an alternative to natural hydrocarbons is growing, which stimulates the studies directed on the involvement in the economic turnover of vast resources of technical lignins as a source of a wide range of compounds and materials with a high added value.[1,2] The works dealing with the studies of the aromatic biopolymer reactivity in such processes as modification by the introduction of new functional groups in the macromolecule structure, depolymerization, synthesis of polymeric composites, *etc.*, acquire the relevance. Since the overwhelming majority of the mentioned reactions are carried out in solutions, the influence of solvents on physicochemical properties and reactivity of lignin appears to be an important question.[3] In this connection, a special attention should be paid to the phenomenon of a preferential (selective) solvation[4] of the polymer reaction centers with the individual components of mixed solvents, which are most frequently used in the lignin chemistry. They include first of all the binary mixtures of water with such highly basic aprotic solvents as DMSO, DMF, 1,4-dioxane (DO), acetonitrile (MeCN), which possess a high dissolving ability toward the natural aromatic polymer and related phenolic compounds.

Taking into account the structural irregularity of lignin macromolecule and the presence in it of phenylpropane units with different substituents *para* to the phenol hydroxy group, it seems logical to study specific features of solvation not the polymer as a whole, but its main structural units using the corresponding model compounds. First of all, we are talking about guaiacol (2-methoxyphenol) *para*-derivatives, bearing carbon-carbon double bonds, alcohol hydroxy, carbonyl, and carboxy groups in the substituent.

In the case of solutions of phenols in mixed solvents, UV absorption spectroscopy is one of the most efficient methods for the studies of preferential solvation processes,[5] since these compounds demonstrate noticeable solvatochromism of the long wavelength benzoid absorption band: the change of water for an aprotic solvent usually leads to the bathochromic shifts from several nanometers (in the case of nondissociated phenol group) to several dozens of nanometers (in the case of phenolate anions).[6,7]

The electron transition energy (and therefore, the position of the band in the spectrum) is determined by the closest solvation surrounding of the chromophore,[8] being a linear function of the molar fractions of the solvent components in the solvation shell. Earlier, for the solutions of a wide range of phenols in the water—*N*,*N*-dimethylformamide[7] solvent system, as well as for the lignin samples in the mixed solvents,[9] we showed that the influence of the solvent on the absorption band position of a certain com-

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pound can be correctly described only based on the preferential solvation models, which take into account the presence in the solvation shell not only the molecules of water (S_1) and an aprotic solvent (S_2), but also at least of their equimolecular complex or a "mixed solvent" (S_{12}).[10—12] The latter can be also considered as a hypothetical structure, whose introduction allows one to take into account the synergetic effect of water and an organic cosolvent on the state of a dissolved compound.[8] In this case, the absorption band position in the binary solvent can be written as:

$$\nu_{\text{mix}} = x_1\tilde{\nu}_1 + x_2\tilde{\nu}_2 + x_{12}\tilde{\nu}_{12}, \qquad (1)$$

where x_i is the molar fraction of the i-kind solvent species in the first solvation sphere, $\tilde{\nu}_i$ is the absorption band position in the corresponding pure solvents and a hypothetical "mixed solvent" consisting only of of complex S_{12} species.

Postulating the formation of complex S_{12} not in the solvent, but directly in the solvation shell of the dissolved compound A, the scheme of the solvation equilibria can be written as:[8]

$$A(S_1)_2 + S_2 \rightleftarrows AS_{12} + S_1$$

$$A(S_1)_2 + 2\,S_2 \rightleftarrows A(S_2)_2 + 2\,S_1\,,$$

which are characterized by the parameters of preferential solvation $f_{12/1}$ and $f_{2/1}$, reflecting a predominance in the solvation shell of, respectively, the "mixed solvent" and solvent S_2 compared to the bulk solution:

$$f_{12/1} = \frac{x_1^0 x_{12}^0}{x_2^0 x_1},\ f_{2/1} = \frac{(x_1^0)^2 x_2}{(x_2^0)^2 x_1}, \qquad (2)$$

where $x^0{}_1$ and $x^0{}_2$ are the molar fractions of components in the initial binary solvent.

Introducing the notation

$$X = x^0{}_2/x^0{}_1$$

and taking into account that the sum of the molar fractions of three components of the solvation shell is equal to 1, the x_1, x_2, and x_{12} values can be found from Eq. (2):

$$x_1 = \frac{1}{1 + f_{12/1}X + f_{2/1}X^2}, \qquad (3)$$

$$x_{12} = \frac{f_{12/1}X}{1 + f_{12/1}X + f_{2/1}X^2}, \qquad (4)$$

$$x_2 = \frac{f_{2/1}X^2}{1 + f_{12/1}X + f_{2/1}X^2}. \qquad (5)$$

Inserting Eqs (3—5) into expression (2), one can easily obtain the absorption band position in a binary solvent:[9]

$$\tilde{\nu}_{\max} = \frac{\tilde{\nu}_1 + \tilde{\nu}_{12}f_{12/1}X + \tilde{\nu}_2 f_{2/1}X^2}{1 + f_{12/1}X + f_{2/1}X^2} \qquad (6)$$

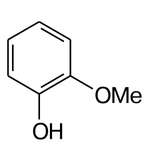
Equation (6) contains three variables ($f_{12/1}$, $f_{2/1}$, and $\tilde{\nu}_{12}$), which can be determined with a high degree of confidence by regression analysis of the experimental data on the dependence of the band position on the solvent composition, provided that ten or more points are available.

Experimental

2-Methoxyphenol (guaiacol, **1**) and four its derivatives differing in the substituent at *para*-position to the phenol hydroxy group, *viz.*, vanillin (**2**), eugenol (**3**), α-guaiacylpropanol (1-(4-hydroxy-3-methoxyphenyl)propan-1-ol, **4**), and ferulic acid (**5**), were used in the work.

α-Guaiacylpropanol was synthesized from vanillin using the Grignard reaction with ethylmagnesium bromide.[13] The purity of the preparation obtained was controlled by its melting point (80—81 °C) and IR spectroscopy (the absence of the absorption band for the carbonyl group). Remaining phenols were used without additional purification as commercially available reagents (the content of the main compound was ≥98%) purchased from Fluka and Sigma-Aldrich. Mixed solvents were prepared by gravimetric method from dimethyl sulfoxide (reagent grade), acetonitrile (high purity grade), 1,4-dioxane (analytical grade), and water of high purity obtained using a Simplicity UV system (Millipore, France). To alkalize the medium for the recording of absorption spectra of anions, a 40% aqueous solution of tetraethylammonium hydroxide (reagent grade, Fluka) was added to the concentration of 0.01 mol L^{-1}. When acidic forms of compounds bearing groups with low pK_a values (vanillin and ferulic acid) were studied, the dissociation was suppressed by the addition of aq. HCl with the background concentration of 0.01 mol L^{-1}.

Absorption spectra were recorded at 25±0.1 °C in a temperature-controlled (using an external water thermostat) quartz cell (l = 1 cm) within the 240—450 nm wavelength range on a Specord-250 Plus double-beam spectrophotometer (Analytik Jena AG, Germany) at the spectral slit width of 1 nm. The distance between the measured points in the spectra was 0.1 nm, the signal in each point was integrated within 1 s. Immediately



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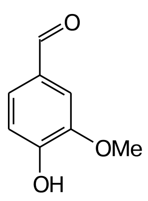

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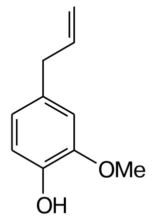

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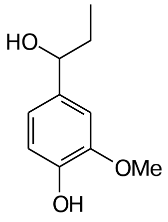

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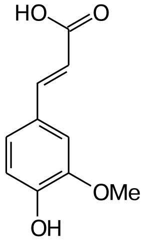

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before measurements, the appliance was calibrated using an incorporated holmium light filter until the absolute accuracy of wavelength measurements was no less than 0.05 nm. Each spectrum was recorded at least three times with subsequent Golay—Savitsky smoothing and determination of the positions of absorption maxima.

Regression analysis of the dependences of positions of absorption bands on the solvent composition was carried out using the CurveExpert version 1.4 program (Daniel Hyams, USA).

Results and Discussion

The experimental data on the dependence of the position of the long wavelength absorption band of phenols under study, which corresponds to the transition of aromatic π-electrons to the excited state (π→π*), on the solvent composition are shown in Fig. 1. In all the cases, one can observe considerable deviations from the ideality (deviations from a straight line), indicating the presence of the preferential solvation effects exhibited by one of the components of the mixed solvent. This is most characteristic of the mixtures of water with 1,4-dioxane, distinguished by the extremely low dielectric permittivity ($\varepsilon = 2.21$ at 298 K), as well as of the water—acetonitrile solvent mixture. In these mixtures, the dependence of $\tilde{\nu}_{\max}$ for the most polar phenols on the molar fraction of organic cosolvent is of a profound extreme character. Generally, the shapes of the curves in Fig. 1 correspond to the results obtained for the water—*N*,*N*-dimethylformamide solvent system,[7] which confirms the necessity to use the model of preferential solvation for their description, since it takes into account the presence in the solvation shell of the dissolved compound of not only the molecules of water and an aprotic solvent, but also of the "mixed solvent" molecule in accordance with the scheme of equilibria suggested by us. From these positions, the presence of extrema on the diagrams for ferulic acid and vanillin is explained by the fact that in the hypothetical binary solvent consisting of only equimolecular complexes with DMSO, DO, or MeCN, the absorption bands of these phenols are considerably shifted toward the region of long wavelengths as compared to the corresponding pure solvents. The reason for this phenomenon can be a bifunctional nature of chromophores in compounds in question, which contain a phenol hydroxy group and a carbonyl group conjugated with the aromatic ring, which serve as a donor and an acceptor of hydrogen bonds, respectively. The solvation of such structures with clusters containing molecules of water and highly basic aprotic solvents, the structure and properties of which strongly differ from the components of which they are formed,[14—17] leads to the relative stabilization of the electronic excited state of the molecule as compared to the ground state and, as a consequence, to the bathochromic shift of the absorption band in the electronic spectrum. This suggestion is additionally confirmed by the absence of the extrema in the dependences of $\tilde{\nu}_{\max}$ on the solvent composition for the anionic forms of compounds under study, containing no proton donor groups.

The results of the regression analysis of the experimental data using Eq. (6) are given in Tables 1—3. Attention should be paid to the correlation coefficients *r*, in all the cases exceeding 0.99 and indicating the adequacy of the mathematical model used.

The coefficients $f_{2/1}$ in all the media under study radically differ for the phenols in molecular form and the corresponding phenolate anions, with the second, as a rule, having $f_{2/1} < 1$. This means that DMSO, MeCN, and DO belong to the class of NDHB-solvents (not donors of hydrogen bonds), which virtually cannot solvate anions. It is interesting that coefficients $f_{2/1}$ for anions do not correlate with acidity (proton donor ability) of the solvent, the minimal parameter values are characteristic of DMSO, while dioxane shows the best solvation ability. This can be apparently explained by a considerable contribution in the free energy of solvation, besides donor-acceptor interactions, of nonspecific hydrophobic interactions. Similarly, for the nondissociated phenol molecules the preferential solvation with an organic component of the mixed solvent in the water—DMSO system is more pronounced for the most polar components (vanillin and ferulic acid), while in the water-dioxane medium for all the guaiacol derivative $f_{2/1} >> 1$.

It is obvious that the complex water—aprotic solvent, possessing a high solvation ability toward both the phenols and the corresponding phenolate anions, demonstrated a pronounced synergetic effect upon interaction with dissolved compounds. It should be noted that parameters $f_{12/1}$ for the neutral and the ionic forms are comparable virtually for all the compounds under study. The solvents differ in the solvating abilities of complexes water—aprotic solvent toward phenols, which increase in the order: dimethyl sulfoxide < acetonitrile < 1,4-dioxane. In the case of phenolate anions, this sequence of solvents is characteristic of only α-guaiacylpropanol and ferulic acid, for the remaining compounds the maximal $f_{12/1}$ values are observed in the water—acetonitrile solvent system.

Table 4 summarizes the coordinates of the maxima for the dependences of the "mixed solvent" content in the solvation shell on the composition of a bulk solution calculated using Eq. (4). From the data obtained, it follows that the complexes of water with DMSO, MeCN, and DO within a certain range of compositions of the binary solvent play the role of the main solvating species. Their fraction in the closest solvation surrounding of phenols under study reaches 29—77%, whereas for the phenolate anions this index lie within 66—96%. For the most polar compound in the anionic form containing carbonyl and carboxy groups (vanillin, ferulic acid), a virtually complete substitution of the solvent components with their equimolecular complex is observed, this is especially true

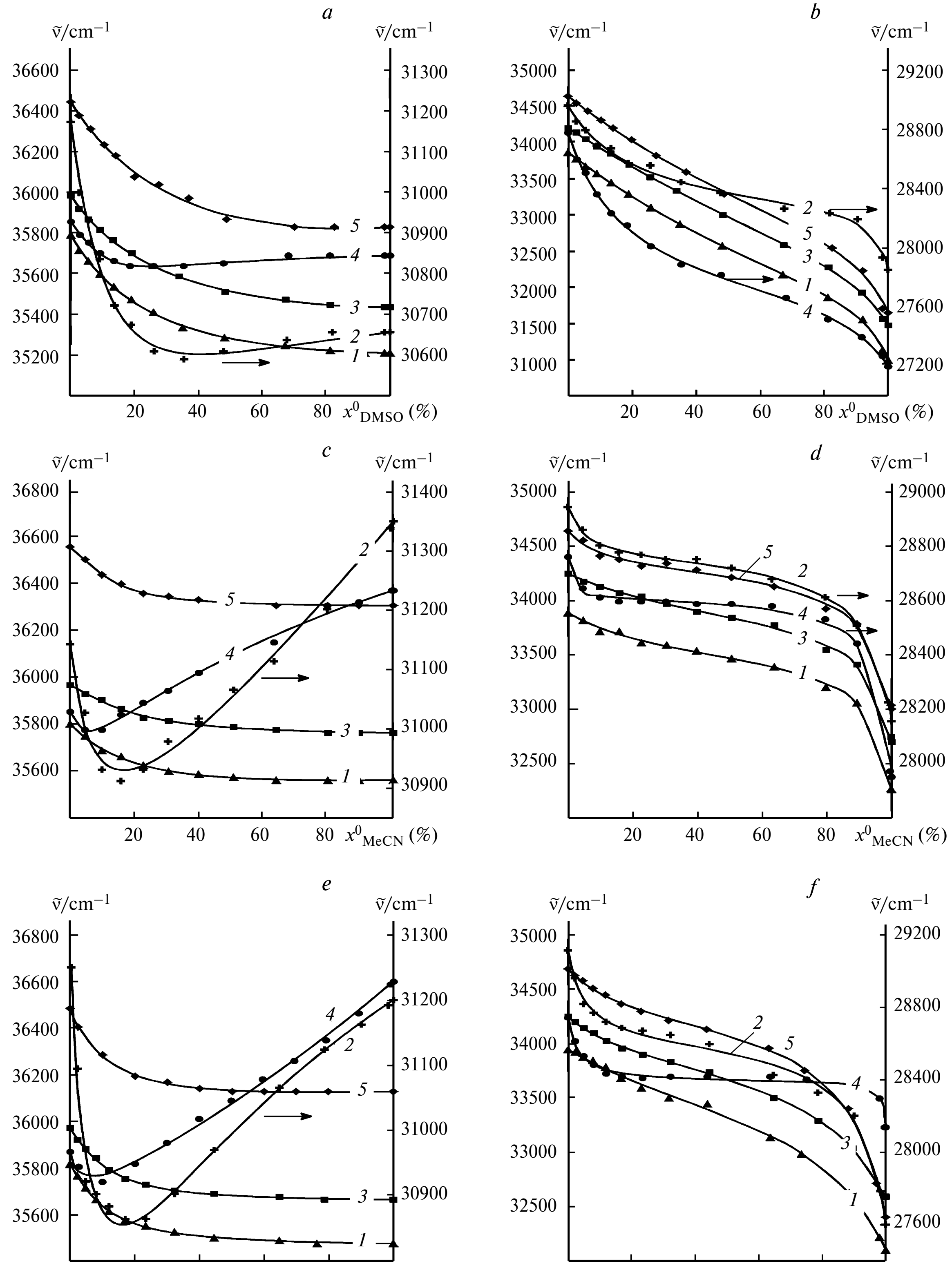

Fig. 1. The dependence of eugenol (*1*), ferulic acid (*2*), α-guaiacylpropanol (*3*), vanillin (*4*), and guaiacol (*5*) absorption band positions in the molecular (*a, c, e*) and the anionic (*b, d, f*) forms on the molar fraction (x^0, %) of the aprotic solvent in the mixtures of water with DMSO (*a, b*), acetonitrile (MeCN) (*c, d*), and dioxane (DO) (*e, f*). The dots reflect the experimental data, the lines represent the results calculated using Eq. (6). On the right ordinate axis, there are given the ν values for ferulic acid (curve *2*, Figs *a—f*) and vanillin (curve *4*, Figs *b, d*, and *f*).

Table 1. Parameters of preferential solvation of guaiacylic phenols in the water—DMSO solvent system

Compound	Form	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_{12}$	$f_{12/1}$	$f_{2/1}$	r
		/cm^{-1}					
Guaiacol	ArOH	36443	35829	35768	3.73	2.270	0.999
	ArO$^-$	34638	31650	32730	1.83	0.196	0.999
Eugenol	ArOH	35791	35211	35239	4.95	4.130	1.000
	ArO$^-$	33864	31000	31897	1.75	0.138	1.000
α-Guaiacylpropanol	ArOH	35984	35436	35440	4.31	2.040	1.000
	ArO$^-$	34200	31480	32380	1.59	0.189	1.000
Vanillin	ArOH	32415	32258	31686	4.02	24.60	0.995
	ArO$^-$	28777	27200	27717	6.32	0.988	1.000
Ferulic acid	ArOH	31172	30656	30385	7.60	22.50	0.996
	ArO$^-$	28960	27850	28291	5.60	0.289	0.996

Note. Index 1 is water, 2 is DMSO.

Table 2. Parameters of preferential solvation of guaiacylic phenols in the water—acetonitrile solvent system

Compound	Form	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_{12}$	$f_{12/1}$	$f_{2/1}$	r
		/cm^{-1}					
Guaiacol	ArOH	36443	36310	36428	6.52	63.30	0.999
	ArO$^-$	34638	33000	34270	9.60	0.808	0.994
Eugenol	ArOH	35791	35562	35548	5.66	8.860	0.999
	ArO$^-$	33864	32260	33443	4.02	0.265	0.999
α-Guaiacylpropanol	ArOH	35984	35765	35854	5.86	25.60	0.998
	ArO$^-$	34200	32800	33783	2.87	0.211	0.999
Vanillin	ArOH	32415	32730	32184	21.1	26.40	0.997
	ArO$^-$	28777	27950	28608	98.6	4.230	0.997
Ferulic acid	ArOH	31172	31350	30779	13.9	12.50	0.993
	ArO$^-$	28960	28155	28752	19.4	1.600	0.999

Note. Index 1 is water, 2 is acetonitrile.

Table 3. Parameters of preferential solvation of guaiacylic phenols in the water—dioxane solvent system

Compound	Form	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_{12}$	$f_{12/1}$	$f_{2/1}$	r
		/cm^{-1}					
Guaiacol	ArOH	36443	36127	36100	9.01	13.40	0.999
	ArO$^-$	34638	32400	34168	6.25	0.717	0.999
Eugenol	ArOH	35791	35474	35609	11.1	74.50	1.000
	ArO$^-$	33864	32100	33354	2.97	0.582	0.999
α-Guaiacylpropanol	ArOH	35984	35663	35731	8.98	42.80	0.999
	ArO$^-$	34200	32590	33801	5.97	1.260	1.000
Vanillin	ArOH	32415	33035	32169	25.7	14.80	0.996
	ArO$^-$	28777	28137	28392	32.9	0.379	0.992
Ferulic acid	ArOH	31172	31200	30620	17.2	30.20	0.990
	ArO$^-$	28960	27600	28599	20.3	1.700	0.996

Note. Index 1 is water, 2 is dioxane.

Table 4. The maximal fraction (%) of the complex water—aprotic solvent in the solvation shell of lignin related phenols

Compound	Form	DMSO		MeCN		DO	
		$x^0_{2\max}$	$x_{12\max}$	$x^0_{2\max}$	$x_{12\max}$	$x^0_{2\max}$	$x_{12\max}$
Guaiacol	ArOH	40	55.3	11	29.1	21	55.2
	ArO$^-$	69	67.4	53	84.2	54	78.7
Eugenol	ArOH	33	54.9	25	48.7	10	39.1
	ArO$^-$	73	70.2	66	79.6	57	66.1
α-Guaiacylpropanol	ArOH	41	60.1	17	36.7	13	40.7
	ArO$^-$	70	64.6	69	75.7	47	72.7
Vanillin	ArOH	17	28.8	16	67.2	21	77.0
	ArO$^-$	50	76.1	33	96.0	62	96.4
Ferulic acid	ArOH	17	44.5	22	66.3	15	61.0
	ArO$^-$	65	83.9	44	88.5	43	88.6

for the mixtures of water with the less polar liquids, acetonitrile and 1,4-dioxane.

In conclusion, the results obtained in these studies indicate a pronounced presence of the preferential solvation in solutions of lignin related phenols in the binary mixtures of water with dimethyl sulfoxide, acetonitrile, and 1,4-dioxane. A special attention should be paid to the synergetic effect arising due to the presence in the solvation shells of guaiacylic phenols of complexes of water with aprotic solvents, which possess high solvation ability toward both the neutral molecules and the corresponding phenolate anions. This phenomenon should be taken into account to better understand effects of medium in the processes of dissolution of lignins and related compounds, acid-base equilibria of lignin phenols, and alternation of their reactivity in solutions.

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