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Solvent Effect on the Acidity Constants of Lignin-Related Phenols in Water–Acetone and Water–1,4-Dioxane Binary Mixtures within the Kamlet–Taft Formalism

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Abstract—Multiparameter regression analysis combined with the principle of liner solvation energies relationship was applied to assess the solvent effect on the acidity of the lignin-related phenols in water–dioxane and water–acetone systems. The coefficients *a*, *b,* and *s* of the Kamlet–Taft equation were calculated taking into account the contributions of different types of solute–solvent interactions to the protolytic properties of the phenols of the guaiacol series.

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Lignin is the second most common natural material on earth, comprising a quarter to a third of the total plant biomass. Despite this, at present, only a small part of its production is involved in technological processes. Being a by-product in cellulose manufacture, it is used mainly as a fuel. Prospects for the use of lignin to produce a wide range of valuable products are related to studies of reactivity of the natural polymer and related phenolic compounds, which is largely determined by the possibility of acid ionization of the phenolic hydroxy group to form phenoxide anion, and, further, the quinomethide structures [1, 2].

As the most effective means to purposefully affect the protolytic properties of phenols the variations in the solvent composition can be regarded especially when using binary mixtures of water with aprotic solvents, which can alter the dissociation constants of phenolic groups by 5–8 orders of magnitude [3]. Among the aprotic solvent of greatest interest are acetone and 1,4-dioxane, which have a high dissolving power in relation to phenolic compounds due to the high basicity. These solvents are widely used in the chemistry of plant materials in pure form and in mixtures with water. Earlier [4, 5], using the methods of spectrophotometric and potentiometric titration, we have determined the constants of acid dissociation in water–acetone and water–dioxane solvents of a wide range of phenols of the guaiacol series that simulate the structural fragments of the coniferous lignin macromolecule. We found that the pK_a dependence on the mole fraction of organic solvent is not linear, and could be best described as a fractional–rational function.

Further development of research in this area should be directed to the disclosure of the mechanism of the influence of environment on the protolytic properties of phenolic compounds. When analyzing the effect of a solvent on the equilibrium constants, in most cases the contributions must be considered of different types of solute–solvent interactions, both non-specific and donor–acceptor ones. For this purpose, a phenomenological approach is widely used now based on the correlation equations expressing the dependence of the free energies in the studied process on a set of parameters that characterize various properties of the solvent [6, 7]. The method of Liner solvation energies relationship (LSER) should be recognized as the most successful among the multiparametric quantitative methods [8], which uses empirical solvato-chromic parameters of solvent polarity α, β, and π^* introduced by Kamlet and Taft [9–11] and characterizing respectively the ability of the solvent to act as the hydrogen bond donor (acidity) or acceptor (basicity), and ability of the solvent to nonspecific interactions (dielectric constant/polarizability). The Kamlet–Taft formalism has been widely used in various studies to describe the effect of environment on the protolytic properties of solutes in non-aqueous and mixed solvents, including water–aprotic solvent mixtures [12–14]. In the latter case the Kamlet–Taft equation is represented as

$$\mathrm{p}K_\mathrm{a} = \mathrm{p}K_\mathrm{a}^0 + s\pi^* + a\alpha + b\beta, \qquad (1)$$

where $\mathrm{p}K_\mathrm{a}^0$ is the acidity constant in an environment with zero values of α, β, and π* (e.g., cyclohexane), *s*, *a*, and *b* are the coefficients taking into account the contributions of the respective types of interactions in the overall effect of the medium.

In the case of aqueous–organic systems, Eq. (1) can be rewritten to eliminate the unknown quantity $\mathrm{p}K_\mathrm{a}^0$ using the numerical values of the solvatochromic polarity parameters for water [14]:

$$\mathrm{p}K_\mathrm{a} = \mathrm{p}K_\mathrm{a}^\mathrm{w} + s(\pi^* - 1.15) + a(\alpha - 1.08) + b(\beta - 0.41), \qquad (2)$$

where $\mathrm{p}K_\mathrm{a}^\mathrm{w}$ is the acidity index in the aqueous medium.

As the objects of investigation we selected the 2-methoxyphenol (guaiacol), and nine of its derivatives to simulate the structural fragments of coniferous lignin macromolecules with various groups in the para position to the phenolic hydroxy group: vanillin (CHO), acetovanillone ($COCH_3$), ferulic acid (CH=CH·COOH), vanillic acid (COOH), vanillic alcohol (CH_2OH), α-guaiacylpropanol ($CHOHC_2H_5$), isoeugenol ($CH{=}CHCH_3$), eugenol ($CH_2CH{=}CH_2$), creosol (CH_3). The acid ionization constants of the compounds in binary mixtures of water with 1,4-dioxane and acetone are taken from the publications [5] and [4], respectively. The values of the Kamlet–Taft polarity parameters of the solvent systems under study are taken from [15–17]. The validity of multiparameter regression analysis largely depends on the amount of processed experimental data. Preliminary calculations showed that in the studied solvent systems, taking into account the availability of $\mathrm{p}K_\mathrm{a}$ for only a limited range of compositions (0–80 wt %) and, consequently, a limited range of parameters of the medium polarity, reproducible results can be obtained by using at least 30 experimental points. Therefore, the $\mathrm{p}K_\mathrm{a}$ values of phenols were interpolated over the aprotic solvent content with the 2% intervals (the Curve Expert 1.3 software) to obtain 40 points. To determine the coefficients *a*, *b* and *s*, we used the method of multiparameter linear regression analysis within the Origin 8.5 software package (the *Multiple regression tool* function).

Tables 1 and 2 list the results of multiparameter linear regression analysis using Eq. (2) for binary mixtures of water with dioxane and acetone, respectively. High values of correlation coefficients (r^2 = 0.996–0.999), as well as the standard deviation σ for the acidity constant indicators, which are at the level of errors of experimental determination of $\mathrm{p}K_\mathrm{a}$, evidence the model validity. An additional visual confirmation of this are the plots of $\mathrm{p}K_\mathrm{a}$ found experimentally (by examples of vanillin, and eugenol) and calculated according to Eq. (2) vs the solvent composition for the water–dioxane (a) and water–acetone (b) systems shown in figure, as well as a comparison of the real and calculated values of the acidity constant indicies $\mathrm{p}K_\mathrm{a}^\mathrm{w}$ of phenols in aqueous solution in the Tables 1 and 2.

Given the complex nature of the parameter $\mathrm{p}K_\mathrm{a}$, which is affected by the energy state of the three types of species in this environment involved in protolytic equilibria, the interpretation of the environment effects within the Kamlet–Taft concept should be based on the features of solvation of undissociated molecules of a phenol, the corresponding phenolate anion, and a proton in the mixed solvent.

For both binary solvents the coefficient *s* is negative, which is consistent with the idea of the influence of dielectric constant on the acidity constant in accordance with the Born model [18].

A particular attention should be paid to the zero value of the coefficient *b* for all the phenols in the water–dioxane system, which indicates the independence of the solvent basicity of the dissociation constants of phenols. A similar result was obtained [13] in the study of acidity constants of substituted phenols in fifteen water–dioxane media. The reason of this phenomenon is, apparently, the proximity of the free energies of transfer of the phenol molecule and a proton from water in water–dioxane mixtures in the studied range of compositions of binary solvent. This effect is not observed in the water–acetone system, and the coefficient *b* for the vast majority of compounds is positive corresponding to the relative “stabilization” of the phenol molecule in comparison with the hydrogen at an increase in the medium basicity. This may be due to a weak change in the Gibbs free energy of the

Table 1. The coefficients of the Kamlet–Taft equation for the dependence of the pK_a of the guaiacol series phenols on the solvatochromic parameters of the binary solvent water–dioxane

Compound	p$K_{aw}^{l\,it}$	p$K_{aw}^{c\,alc}$	Coefficients			σ	r^2
			a	*b*	*s*		
Vanillin	7.40	7.41	–0.37	0	–10.07	0.051	0.998
Acetovanilon	7.81	7.92	–0.80	0	–10.29	0.044	0.998
Ferulic acid, OH_{phenol}	9.38	9.44	–0.52	0	–10.21	0.052	0.998
Vanilic acid, OH_{phenol}	9.39	9.54	–0.69	0	–10.94	0.056	0.998
Vanilic alcohol	9.79	9.92	–0.84	0	–11.03	0.051	0.998
α-Guaiacylpropanol	9.83	9.95	–1.28	0	–10.63	0.035	0.999
Isoeugenol	9.89	10.04	–0.82	0	–11.50	0.035	0.999
Guaiacol	10.04	10.17	–0.96	0	–11.28	0.069	0.997
Eugenol	10.15	10.26	–0.85	0	–11.86	0.052	0.998
Creozol	10.27	10.42	–0.66	0	–12.09	0.064	0.998

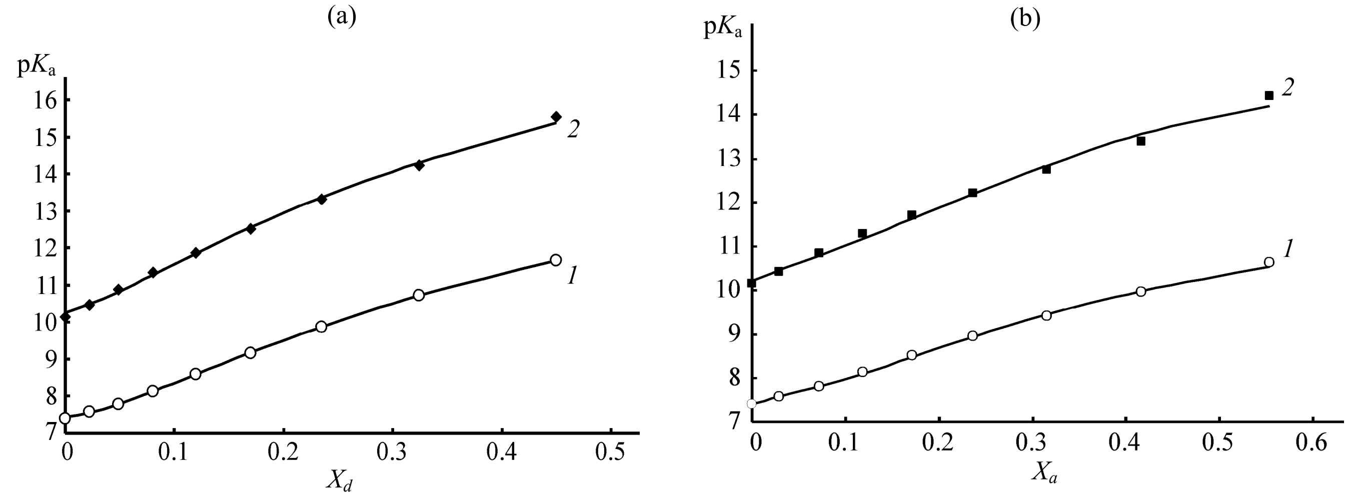
Table 2. The coefficients of Kamlet–Taft equation for the dependence of the pK_a of the guaiacol series phenols on the solvatochromic parameters of the binary solvent water–acetone

Compound	p$K_{aw}^{l\,it}$	p$K_{aw}^{c\,alc}$	Coefficients			σ	r^2
			a	*b*	*s*		
Vanillin	7.40	7.42	–13.08	–8.21	5.49	0.019	0.999
Acetovanilone	7.81	7.83	4.79	6.68	–16.47	0.030	0.999
Ferulic acid, OH_{phenol}	9.38	9.32	1.52	3.74	–14.08	0.040	0.998
Vanilic acid, OH_{phenol}	9.39	9.43	6.05	8.77	–18.92	0.025	0.999
Vanilic alcohol	9.79	9.82	5.75	7.74	–18.75	0.035	0.999
α-Guaiacylpropanol	9.83	9.88	8.90	10.34	–22.28	0.035	0.999
Isoeugenol	9.89	9.94	6.74	8.73	–19.97	0.035	0.999
Guaiacol	10.04	10.07	5.85	7.81	–19.06	0.036	0.999
Eugenol	10.15	10.22	7.61	8.69	–21.55	0.047	0.998
Creozol	10.27	10.33	–8.71	–3.02	–1.39	0.077	0.996

proton in the investigated range of compositions of water–acetone solvent (0–55 mol %) since the introduction of acetone in the solvation shell of the H^+ ion occurs only in the compositions close to the pure organic component [19].

The difference in the signs of the coefficient *a* for the mixtures of water with 1,4-dioxane and acetone is of considerable interest. While for the water–dioxane solutions it takes negative values in correspondence with a decrease in the Gibbs energy of phenoxide anion due to the donor–acceptor interactions with the solvent and the corresponding reduction in the pK_a value, in the water–acetone mixtures anomalous correlation occurs between the dissociation constants and the medium acidity. Still, the positive values of *a* at the study of the protolytic equilibria in the water–aprotic solvent media has been widely reported in the literature, for example, for the water–dioxane solutions [20] or mixtures of water and *N,N*-dimethylformamide [21]. In our opinion, the reason for this phenomenon is a significant difference in the preferential solvation effects of the studied compounds and reference solvatochromic indicators (e.g., Reihardt betaine) used to determine the solvent acidity by Kamlet–Taft [7].

For the majority of compounds in both binary solvents the π* parameter that considers the effect of nonspecific solvation contributes the most significantly, and in the water–dioxane mixtures this con-



The dependence of the pK_a of vanillin (*1*) and eugenol (*2*) on the mole fraction of dioxane (a) and acetone (b) in binary aqueous–organic solvents at 25°C. The points correspond to experimental data, plots are calculated according to Eq. (2).

tribution is absolutely dominant: the *s*/*a* ratio falls to the range from 8 to 27. In the mixtures of water with acetone, in addition to nonspecific interactions, there is a significant contribution from the donor–acceptor interaction of the guaiacol series phenols with the solvent, while the contributions of the medium acidity and basicity in the total effect of changing the pK_a of phenolic hydroxy groups are comparable.

Comparison of the behavior of various phenols with *para*-substituents shows insignificant differences, exceptions are vanilin and creozol in water–acetone mixtures, demonstrating the dominant role of specific interactions with the solvent on their protolytic properties.

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