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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Calorimetric Study of the Interaction between Lignin and Aprotic Solvents

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Abstract—Interaction of lignin with dimethyl formamide, dimethyl sulfoxide, and dioxane was studied by calorimetry. Concentration dependences of the enthalpy of interaction between lignin and aprotic solvents were obtained.

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The promise of calorimetry as a method for studying the structure of lignin and its interaction with solvents was demonstrated as early as in 1970s [1, 2]. However, certain difficulties in experiments with polymers have resulted in that this method failed to gain due acceptance for studies of wood and its macromolecular components.

It was shown in previous thermochemical studies of the lignin–ethanol–water–sodium hydroxide system [3, 4] that the process has exothermic nature primarily associated with the reaction of neutralization of hydroxy groups of lignin with an alkali. The concentration dependences of the enthalpy of dissolution have a maximum whose position depends on the ethanol content in the system. An increase in the concentration of ethanol or sodium hydroxide in the system exerts the same influence by enhancing the exothermic nature of the interaction process.

Aprotic organic solvents, such as dimethyl sulfoxide (DMSO), dimethyl formamide (DMFA), and dioxane are widely used for recovery of lignin from wood and analysis of its properties.

The aim of this study was to determine the enthalpy of interaction between lignin and aprotic solvents by calorimetry and make a comparative analysis of the behavior of lignin in solvents of varied nature.

EXPERIMENTAL

As object of study was taken a preparation of fir-tree sulfate lignin (SL) with a mass-average molecular weight of 10740 and the following functional composition (%): groups: methoxy 11.9, carbonyl 3.8, general acidic 6.8, phenol hydroxy 4.6, carboxy 2.2; sulfur 1.8. DMSO, DMFA and dioxane of chemically pure grade served as solvents.

The enthalpy of interaction between lignin and a solvent was determined on an MKDP-2 differential microcalorimeter by the method described in [4].

The concentration dependences of the specific enthalpy ΔH_{sp} of lignin interaction with DMSO and DMFA, obtained in the lignin concentration range in solution of 10–60 g/1000 g of solvent, are linear (Fig. 1). For the SL–dioxane system, ΔHsp is nearly concentration-independent, $\Delta H_{\text{sp}} = -41.8 \pm 2.5$ J g^{-1}. A similar phenomenon was observed in interaction of coniferous dioxane-lignin with dioxane [5]. On the whole, the process of SL interaction with organic solvents is exothermic.

It was found by the example of DMSO how introduction of water, in which SL is almost insoluble, into the system affects the interaction of lignin with solvents. It was possible to introduce 30% H_2O into the system without loss of its dissolving capacity. As the content of the organic solvent was reduced to 60%, lignin became insoluble in the DMSO–water system in the concentration range under study. The concentration dependences of ΔH_{sp} are also linear (Fig. 2), which makes it possible to determine the first integral enthalpies of the interaction, ΔH_0. Values of ΔH_0 for the aprotic solvents studied and mixtures of DMSO and water are listed in the table. As the DMSO concentration increases, the exothermicity of the interaction between SL and water linearly grows (Fig. 3).

A decrease in the fraction of water in the system makes the polarity of the solvent lower ($\varepsilon_{water} = 78.3$, $\varepsilon_{DMSO} = 49.0$), and polyelectrolyte effects weaker. In this case, lignin forms more loose structures, which favor solvation, a process of exothermic nature.

Because the interaction of lignin with a solvent is governed by a number of processes (swelling, solvation, association, etc.) and by the different extents of solvent penetration into the macromolecular coil, interpretation of reasons why the enthalpy of the system changes is always difficult. Compounds modeling the structural unit of lignin are traditionally used in chemistry of lignin to analyze processes unrelated to its macromolecular properties. In the present study, vanillin is used as the model substance. It was found that the interaction of vanillin with DMSO, DMFA, and dioxane is endothermic and the enthalpy of interaction, almost independent of the vanillin concentration, has the following values (kJ mol-1): 8.15 ± 0.12 in DMSO, 7.04 ± 0.43 in DMFA, and 14.86 ± 2.12 in dioxane. The positive values of the enthalpy for all the solvents studied are due to the energy expenditure for disintegration of the crystal lattice of vanillin. Presumably, this component substantially exceeds the exothermic contribution of solvation to the overall effect of the process. Thus, use of a low-molecular-weight analog of the structural unit of lignin in analysis of its interaction with aprotic solvents fails to furnish helpful information, in contrast to a study of processes in the water–ethanol–NaOH system [3, 4], in which the predominant contribution to the total enthalpy of interactions both with lignin preparations and with models of its structural unit is made by the reaction of neutralization of the phenol hydroxyl.

The organic solvents used in the study are aprotic, but dioxane markedly differs in its properties from DMSO and DMFA. It is substantially less polar and has lower values of the dielectric constant, dipole moment, and donor number DN_{SbCl_5} [6]. These differences in the properties of solvents belonging to the same class are manifested in their interaction with lignin. Although the interaction is exothermic in all cases, there is no concentration dependence of the enthalpy of interaction for dioxane ($\Delta H_{sp} = -41.8 \pm 2.5$ J g^{-1}), whereas for DMFA and DMSO, the enthalpy of interaction linearly increases with the concentration and reaches the value of ΔH_{sp} for the SL–dioxane system only for the most concentrated solutions.

First integral enthalpy ΔH_0 of SL interaction with DMSO, DMFA, dioxane, and DMSO–water mixtures

Solvent	$-\Delta H_0$, J g^{-1}
DMFA	92.9
Dioxane	41.8
DMSO	103.4
DMSO + H_2O, %:	
5	95.2
10	74.9
20	60.5
30	43.6

Because it is known that, from the thermodynamic standpoint [7], dioxane is the worst of the lignin solvents studied, it can be assumed that stable associates of macromolecules are formed in solution even at low lignin concentrations. In DMSO and DMFA, associates of this kind are formed only at comparatively high lignin

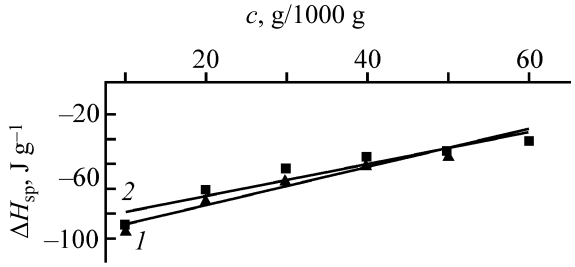

Fig. 1. Specific enthalpy ΔH_{sp} of SL interaction with (*1*) DMSO and (*2*) DMFA vs. SL concentration *c*.

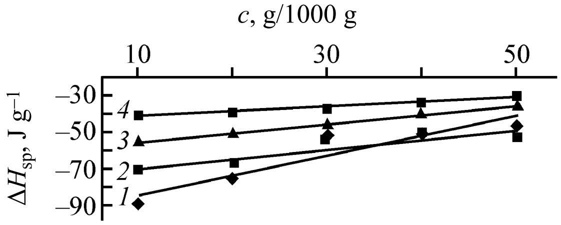

Fig. 2. Specific enthalpy ΔH_{sp} of SL interaction with DMSO–water systems of various compositions vs. the SL concentration *c*. Water content (%): (*1*) 5, (*2*) 10, (*3*) 20, and (*4*) 30.

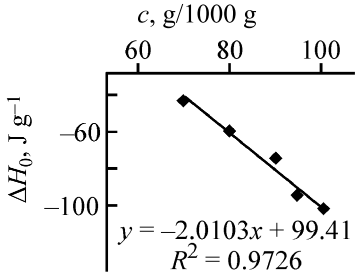

Fig. 3. First integral enthalpy ΔH_0 of SL interaction with the solvent vs. the DMSO concentration c in the DMSO–water system.

concentrations. The fact that the exothermicity of the process of SL interaction with DMSO and DMFA becomes higher as the SL concentration decreases can be accounted for not only by the increase in the negative solvation component of the enthalpy of interaction, but also by conformational transformations of the macromolecule in good solvents (formation of conformers of large hydrodynamic size, with a large solvation shell, upon a decrease in the lignin concentration has been revealed by laser correlation spectroscopy [8]), which can produce a noticeable energy effects.

CONCLUSIONS

(1) The process of interaction between the fir-tree sulfate lignin and organic aprotic solvents is exothermic. For dioxane, the enthalpy of interaction is almost independent of the lignin concentration, whereas for dimethyl sulfoxide and dimethyl formamide, the concentration dependences are linear.

(2) Replacement of a part of the organic solvent (up to 30% for dimethyl sulfoxide) with water makes the exothermicity of the interaction lower, because the thermodynamic quality of the solvent becomes poorer.

(3) A study of the system vanillin–aprotic solvent demonstrated that the main contribution to the enthalpy of interaction comes from endothermic processes of disintegration of the crystal lattice of a low-molecular-weight compound modeling the structural unit of lignin, with solvation processes manifested to an insignificant extent.

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