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THERMODYNAMICS OF THE MIXING OF LIGNIN-CONTAINING COMPOSITIONS

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The thermodynamic mixing parameters in the composition nitrolignin—hydrolyzed nitron have been determined and it has been shown that the system is thermodynamically stable over the whole range of compositions.

In the literature, great attention is devoted to chemical reactions taking place between macromolecules. Interest in them is due both to the possibility of using such reactions for modeling processes taking place in biological systems and also to the practically useful properties of the products of these reactions.

We have investigated the two-component polymer system consisting of nitrolignin (NL) and alkali-hydrolyzed nitron [polyacrylonitrile] (N). It is known that the composition NL-N possesses biological activity, stimulating the growth and development of plants [1]. In the practical use of such complex polymer systems, questions of their reliability inevitably arise, which is unambiguously connected with their thermodynamic stability or the compatibility of the polymers with one another.

At constant pressure and temperature, thermodynamic stability can be evaluated from the (Gibbs) free energy of mixing of the polymers, G_{mix} [2]. To determine G_{mix}, we have studied the isothermal sorption of water vapor on samples of the initial components, NL and N, and of their mixtures in various ratios.

Figure 1 shows absorption isotherms of the samples investigated. All the isotherms obtained were concave in relation to the axis of ordinates, which is characteristic for dense-packed polymers [3]. Over the whole range of relative pressures $p/p°$ the sorption capacity of nitrolignin was lower than that of N. This is explained by the fact that N is a linear polymer, while nitrolignin consists of a greatly condensed macromolecule with a high packing density.

The sorption isotherms of the mixtures of polymers were located between the sorption isotherms of the individual polymers. It may be mentioned that with an increase in the nitrolignin content of the system, the sorption capacity of the mixture fell. This is probably explained by the fact that at a low NL:L ratio there is a binding of the linear chains of N with the compact molecules of nitrolignin, which leads to the formation of a polyelectrolyte complex (PEC) NL—N more densely packed than the initial N.

With an increase in the NL:N ratio, the sorption isotherms of the PECs, while lower than that for pure nitron, were nevertheless higher than that for pure nitrolignin. We may note that in the case of a composition of two linear polymers the formation of PECs leads to a more compact structure than those of the initial components. In the NL—N system, however, no further compactization of the already condensed macromolecules of the initial nitrolignin takes place on it binding into a polyelectrolyte complex.

The sorption isotherms shown in Fig. 1 have been used to calculate the Gibbs energy of mixing g_{mix} of the polymer components [4]. Graphs of the concentration dependence of g_{mix} are given in Fig. 2. It can be seen that N possesses a greater thermodynamic affinity for water than the nitrolignin macromolecules. At the minima of the curves, $g_{\mathrm{mix}}(\mathrm{N}) = 78$ cal/g and $g_{\mathrm{mix}}(\mathrm{NL}) = 32$ cal/g. The values of g_{mix} for mixtures of these polymers lie between the values of g_{mix} for N and NL.

The mean Gibbs energy of mixing g_x was determined by Tager's method [4], for which, from the curves of Fig. 2, we calculated G_{mix} for 1 g of each polymer *G*I and *G*II and for 1 g of mixture with water *G*III. These values were inserted in the equation

$$g_x = G\mathrm{III} - (x_1\, G\mathrm{I} + x_2\, G\mathrm{II}),$$

where x_1 and x_2 are the molar fraction of the components.

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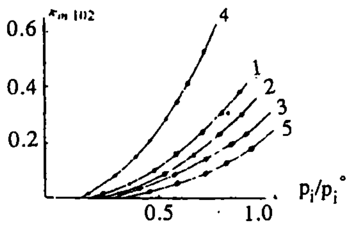

Fig. 1. Isotherms of the sorption of water vapor: N:NL= 2:1 (*1*), 1:1 (*2*), 1:2 (*3*), N (*4*), NL (*5*); *t* = 25°C.

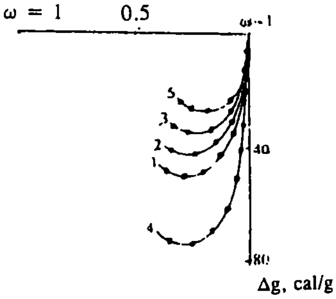

Fig. 2. Dependence of the mean free energy on the composition of the solution: N:NL= 2:1 (*1*), 1:1 (*2*), 1:2 (*3*), N (*4*), NL (*5*); *t* = 25°C.

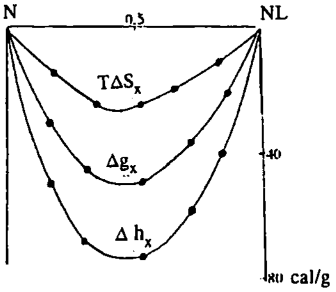

Fig. 3. Dependence of the thermodynamic parameters on the composition of the mixture (t = 25°C).

Figure 3 shows the dependence of the calculated values of g_x on the composition of the polymer compositions. Over the whole range of compositions, the NL−N system is characterized by negative values of g_x, which demonstrates the thermodynamic compatibility of N and nitrolignin.

It is known that the heat of mixing h_x and the entropy of mixing s_x can be determined from the equation

$$g_x = h_x - T\Delta s_x.$$

The isothermal sorption of water was carried out at various temperatures. The sorption isotherms obtained for the NL−N system at 20, 25, and 30°C were similar in nature. Figure 3 shows the dependence of the calculated thermodynamic parameters h_x and $T\Delta s_x$ on the composition. It can be seen that both these magnitudes have negative values over the whole range of compositions. The negative value of h_x witnesses an energetic interaction between the macromolecules. This result confirmed those that we had obtained previously by the methods of potentiometry and gel chromatography [5]. The negative value of $T\Delta s_x$ is a result of an ordering of the mixture.

Thus, the macromolecular system NL−N is thermodynamically stable, which ensures retention of the structure and functional properties of the composition with time.

EXPERIMENTAL

The sorption isotherms were obtained on an apparatus with a McBain spiral balance. The sensitivity of the spirals was 0.5 mm/mg. Water vapor pressure was measured with a U-shaped manometer. The readings of the values to be measure were made with a cathetometer.

The samples for investigation were prepared in the form of thin films obtained from 5% aqueous solutions. The prepared films were dried at room temperature to constant weight.

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