

# THERMODYNAMIC PROPERTIES OF SOLUTIONS OF WATER-SOLUBLE MIXED CELLULOSE ESTERS

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*The thermodynamics of the mixing of water-soluble mixed cellulose esters with water has been studied. A dependence of the affinity of a water-soluble cellulose acetate for water on the nature of a new radical introduced into the macromolecule and the competing interaction of molecules of the same and different types has been shown. Thermodynamic analysis has demonstrated the dominating role of solvation among the various factors determining the interaction of cellulose acetomaleate and acetophthalate with a solvent. A fall in affinity in the cellulose aminoacetate–water system is due to the contribution of entropy effects, leading to an increase in the Flory-Huggins parameter.*

The phenomenon of an increase in the hydrophilic properties of such a polyhydroxy compound as cellulose on a limited substitution of its hydroxy groups by other radicals is due to the existence of a system of strong hydrogen bonds blocking the interaction of cellulose with water but breaking down on partial substitution. However, hydrophilicity is connected not only with the substitution itself but also with the properties of the substituting radical [1, 2]. It was therefore desirable to study the sorption properties and the thermodynamics of the interaction of mixed cellulose esters with water.

We have investigated a water-soluble cellulose acetate (WSCA) with a degree of substitution  $F_{ac} = 0.72$ ; a water-soluble cellulose acetophthalate (WCAP) with  $F_{ac} = 0.72$ ,  $F_{phl} = 0.08$ , OH group content 2.2; a water-soluble acetomaleate (WCAM) with  $F_{ac} = 0.71$ ,  $F_{mal} = 0.06$ , OH group content 2.2, and a water-soluble cellulose aminoacetate (WCAA) with  $F_{ac} = 0.65$ ,  $F_{amino} = 0.51$ , OH group content 1.84. The degree of polymerization of all the specimens studied was  $\sim 200$ .

The sorption of water vapor was studied by means of a McBain spiral balance with a sensitivity of  $\sim 1.3 \cdot 10^{-3}$  m/kg at 293 K and a residual pressure of  $10^{-3}$ – $10^{-4}$  Pa. When the equilibrium values of the amount of water sorbed had been reached, the equilibrium vapor pressure was measured and sorption isotherms were plotted. The heat of mixing was determined in a modernized DAK-I-IA calorimeter. Before the beginning of the experiments, the samples were dried to constant weight and were placed in the working cell of the microcalorimeter. After thermal equilibrium had become established the samples were brought into contact with water vapor. The heat effect was shown on the panel of the integrator and recorded in the form of curves in a diagram.

Figure 1 shows isotherms of the sorption of water vapor for all the samples investigated. As has been shown in [3], the sigmoid form of the curves, with a convex initial section, is due to the simultaneous occurrence of two processes: physical adsorption in the pores of the polymer, and its swelling. It follows from Fig. 1 that mixed cellulose esters have a high sorption capacity in water and that the magnitude of the equilibrium sorption depends on the nature of the substituting radical, decreasing in the sequence WCAM > WCAP > WSCA > WCAA.

The sorption isotherms were used to calculate the thermodynamic affinities of water for the mixed cellulose esters. The difference in the chemical potentials of 1 g of water in the phase of a swollen polymer,  $\Delta\mu_1$ , and of pure water,  $\Delta\mu_1^0$ , was calculated by means of the equation

$$\Delta\mu_1 = \frac{RT}{M_1} \ln \frac{P_1}{P_1^0},$$

where  $M_1$  is the molecular mass of the sorbent.

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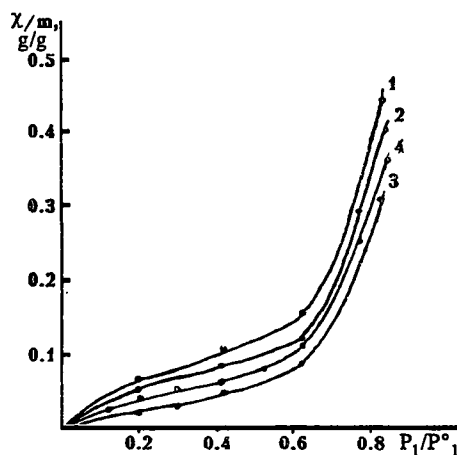


Fig. 1. Isotherms of the sorption of water vapor by water-soluble cellulose esters at 298 K: 1) WCAM; 2) WCAP; 3) WCAA; 4) WSCA.

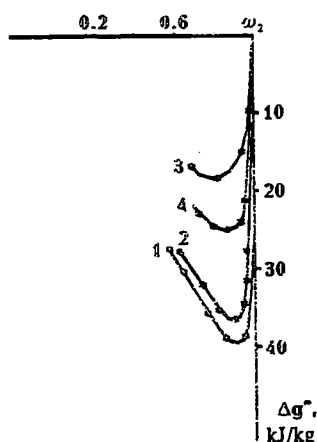


Fig. 2. Concentration dependence of the mean free energy of mixing,  $\Delta g^m$ , of water with: 1) WCAM; 2) WCAP; 3) WCAA; 4) WSCA.

Then, by means of the Gibbs-Duhem equation, the value of  $\Delta\mu_2$  was determined, and, using the equation

$$\Delta g^m = \omega_1 \Delta\mu_1 + \omega_2 \Delta\mu_2$$

the mean Gibbs energy of the mixing of the polymer with water [4].

The dependence of  $\Delta g^m$  on the volume fraction of the polymer in the polymer-water system is shown in Fig. 2. For all the systems studied,  $\Delta g^m < 0$ , i.e., the water sorption process took place spontaneously. However, for cellulose aminoacetate the absolute value of the Gibbs energy decreased as compared with the initial water-soluble cellulose acetate, i.e., the thermodynamic affinity of the polymer for water or its hydrophilicity deteriorated. The introduction of phthaloyl and maleoyl groups into CA considerably increased the affinity of cellulose acetate for water.

It is known that the interaction of cellulose with water is accompanied by an exothermic heat effect [5]. As the investigations have shown, the equilibrium effect of the interaction of water with mixed cellulose esters is also exothermic. However, for cellulose aminoacetate we observed a separation of the total process of the interaction with water into endo and exo effects, taking place with a subsequent enhancement of the exo effect (Table 1).

As a rule, the endothermic effect is accompanied by a disruption of hydrogen bonds in the cellulose on the sorption of water, while the exothermic effect is due to the solvation of the free OH groups formed [6]. The change in the sign of the heat effect on the interaction of WCAA with water apparently takes place as a result of the sequence: solvation — breakage of hydrogen bonds — solvation of free polar groups.

TABLE 1. Heat Effects of the Interaction of Mixed Cellulose Esters with Water at 293 K

Sample	$-\Delta H,$	$+\Delta H,$	$\Sigma\Delta H,$
	kJ/kg		
WCAA	4.4	0.7	-3.7
WCAM	17.9	-	-17.9
WCAP	18.6	-	-18.6

TABLE 2. Thermodynamic Parameters of Mixing for Mixed Cellulose Ester—Water Systems at 293 K

Sample	$\Delta G$	$\Delta H$	$T\Delta S$
	kJ/kg of polymer		
WSCA (init.)	-32.6	-28.2	4.4
WCAM	-46.6	-17.9	28.7
WCAP	-43.7	-18.6	25.1
WCAA	-25.4	-3.7	21.7

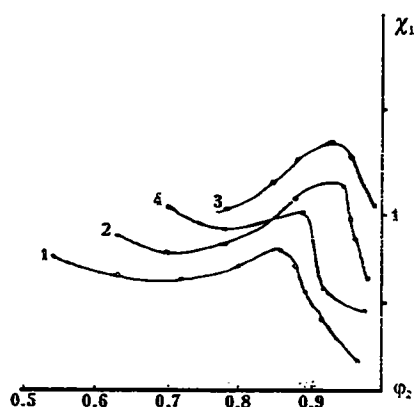


Fig. 3. Dependence of the Flory-Huggins interaction parameter  $\chi_1$  on the volume fraction of a polymer: 1) WCAM; 2) WCAP; 3) WCAA; 4) WSCA.

The difference between the systems investigated is due to the thermodynamic parameters of the interactions, which bear the main information on the mechanism of the interaction and the causes of affinity between the components of the system (Table 2).

As can be seen from Table 2, the ratio of the magnitudes  $\Delta H^m$  and  $T\Delta S^m$  is such that the Gibbs energy of the mixing with water of the cellulose esters investigated is negative over the whole range of compositions, and the form of the concentration dependence witnesses the thermodynamic stability of the solutions (Fig. 2).

An improvement of the dissolving capacity of water for WSCA with the introduction of phthaloyl and maleoyl groups is shown by an increase in the negative values of the energy component of the Gibbs potential and a decrease in the Flory-Huggins interaction parameter  $\chi_1$  (Fig. 3). Direct application of the Flory-Huggins equation to the cellulose esters investigated shows that the magnitude  $\chi_1$  is not a constant but depends on the moisture content, particularly during the initial period of sorption. The  $\chi_1$  value is 0.5 for the maximum dissolving capacity of a liquid. Water is a solvent for the cellulose ester investigated and the value of  $\chi_1$  should lie below 0.5, as is actually observed. These changes are linked with a deviation of the structure of a real solution from that taken in the initial model.

The compatibility of the WCAM—water and WCAP—water systems is determined by the change in the enthalpy factor, and its contribution to the free energy of formation of the system becomes predominating. In this case, high values of  $\Delta H^m$  connected with the energetic interaction between sorbate molecules and active groups of the sorbent determine the preferential localization of the sorbate molecules in space. For the WCAA—water system there is a gain in the free energy of mixing of the solvent with the cellulose ester that is determined mainly by the entropy of mixing. Positive values and a rise in entropy indicate a predominant disordering of the structure of the polymer and of the solvent.

Thus, thermodynamic analysis has shown a dependence of the affinity of the water-soluble cellulose acetate–water system on the introduction of a new group into it and a change in the competing interaction of molecules of the same and different types. The sorption of water in cellulose acetomaleate and acetophthalate is due mainly to the existence of thermodynamic affinity, leading to hydrophilic hydration accompanied by a considerable heat effect. The cellulose aminoacetate–water system is characterized by a weakening of the energetic interaction with an enhancement of entropy effects.

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