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THERMOCHEMICAL CHARACTERISTICS OF SOLUTIONS OF CELLULOSE AND ITS ETHERS AND ESTERS *

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ABSTRACT

Concepts of a new approach to the quantitative evaluation of the thermodynamic parameters of the processes of specific solvation in solutions of cellulose, its ethers and esters on the basis of accounting for the electron donor–acceptor (EDA) ability of polymer and solvent are presented. The dependence between the EDA properties of solvents, the degree of substitution of hydroxyl groups of cellulose by acetate groups, the concentration of polymer and the values of the enthalpies of solution and transfer are analysed. The interrelation between the thermochemical, microdynamic and structural properties is revealed; this allowed them to be considered from the viewpoint of the most important thermodynamic parameters of the solvation processes in solutions of the cellulose derivatives.

INTRODUCTION

Due to their universality, quantitative thermochemical methods are widely used to investigate the properties of solutions of polysaccharides [1,2]. The concept of electron donor–acceptor (EDA) complex formation [3] is now the basic idea explaining the character of the interaction of various organic solvent systems for cellulose and its derivatives. In this connection, calorimetric studies on the specific solvation of polymers in solution and revelation of the interrelation between the values of the enthalpies of solution and the EDA properties of solvents is of considerable interest. Attention was paid to this question by Tsvetkov et al. [4,5]. However, to our mind, the following points were not taken into account. Interpretation of the data on the enthalpies of interaction of cellulose and its derivatives with low-molecular-weight liquids is complicated due to their lack of precision in the thermodynamic plane [1,6]. The electron-donor or electron-acceptor ability of solvents was used when discussing the experimental results. The polyfunctionality of cellulose and its derivatives makes it necessary to take into

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account both the donor and acceptor properties of liquids in total. The literature data on the thermal effects of the solution of polysaccharides characterizing the energetics of the solution process on the molecular level are very few. This provides wide perspectives for investigations in the sphere of the calorimetry of solutions of cellulose and its derivatives.

The aim of the present work is to establish the regularities of the influence of solvent EDA ability, the degree of substitution of hydroxyl groups of cellulose by the acetate groups, the concentration of hydroxypropylcellulose in solutions on the values of the enthalpies of solution, $\Delta H^0_{\mathrm{soln}}$, of cellulose, cellulose acetates and dimethylsulfoxide (low-molecular-weight probe).

EXPERIMENTAL

We measured experimentally using a hermetic isoperibolic microcalorimeter at 298.15 K the enthalpies of solution, $\Delta H^0_{\mathrm{soln}}$, of cellulose and its acetates with different degrees of substitution in trifluoroacetic acid (CF_3COOH) and its mixtures with the chlorinated hydrocarbons 1,2-dichlorethane ($C_2H_4Cl_2$), methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$) (chlorinated hydrocarbon content in mixture was 0.3 mol fraction), dimethylacetamide (DMAA), dimethylformamide (DMFA), dimethylsulfoxide (DMSO). We also determined the $\Delta H^0_{\mathrm{soln}}$ of DMSO in solutions of hydroxypropylcellulose (HOPC) in water, DMAA, DMFA, 1,4-dioxane (DO), ethanol over $0–7.0 \times 10^{-5}$ mol fraction polymer concentration intervals.

We used samples of wood cellulose (C) and its acetates synthesized on experimental units of the scientific-industrial enterprise “Polimersintez” (Vladimir) with an average degree of polymerization of 400 and degrees of substitution of 1.66 (AC), 2.38 (DAC) and 2.90 (TAC). The Röntgenostructural analysis according to the technique described by Nilson [7] was used to determine the degree of crystallinity of polymers. The degrees of crystallinity of C, AC, DAC and TAC were equal to 0.59, 0.42, 0.44 and 0.43, respectively. We used HOPC of the “J” type, “Klucel” (U.S.A.) with a molecular mass 120 000 and a degree of mole substitution 3.0. The polymer samples were dried in vacuo without additional purification for 24 h at 330 K. The solvents were prepared according to the techniques described elsewhere [8,9]. Mixed solvents and HOPC solutions were prepared gravimetrically. The technique of measuring the thermal effects of solution of polysaccharides is given elsewhere [10]. The error of the thermochemical measurements was 1–2%.

RESULTS AND DISCUSSION

Figure 1 shows the dependences of the thermal effects of solutions of C, AC, DAC and TAC on the degree of substitution of the hydroxyl groups by

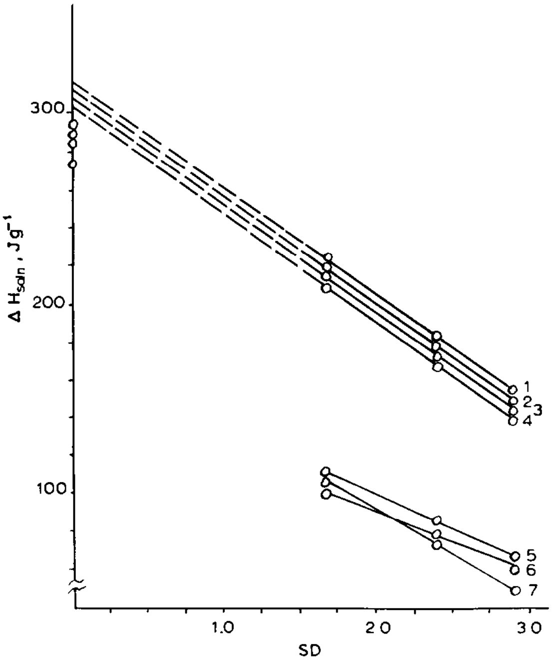

Fig. 1. Dependences of the enthalpies of solution of C, AC, DAC and TAC on the degree of substitution of hydroxyl groups by acetate groups in $CF_3COOH+C_2H_4Cl_2$ (1), $CF_3COOH+CH_2Cl_2$ (2), $CF_3COOH+CHCl_3$ (3), CF_3COOH (4), DMSO (5), DMFA (6), and DMAA (7).

acetate groups in non-aqueous individual and mixed solvents at 298.15 K. As one can see, there is a linear dependence between the values of the solution enthalpies and the amount of acetic acid in the cellulose acetates for all the solvents studied. The increase in exothermicity of solutions of the cellulose acetates in non-aqueous solvents with decreasing degree of substitution is determined by the rise in the EDA ability of the polymers.

It is known that in thermochemical studies on the processes of solutions of cellulose and its derivatives, one should take into account the energetic contributions related to the melting of the crystalline regions of polymers (ΔH_{melt}) and of the transition of their glass-like regions into a highly elastic state under the action of solvents (ΔH_{gl}). According to some data [4] the values of ΔH_{melt} and ΔH_{gl} for cellulose are equal to 13.4 and -12.6 kJ (mol elem-link)$^{-1}$, respectively, i.e. in the case of our samples with a degree of crystallinity 0.59, the contributions from ΔH_{melt} and ΔH_{gl} compensate each other to a great extent. We believe that this can also apply to the cellulose acetate samples. In this connection, ΔH^0_{soln} characterizes mainly the process of the specific solvation of polymers and their absolute values are determined by the donor–acceptor properties of the components of the solution.

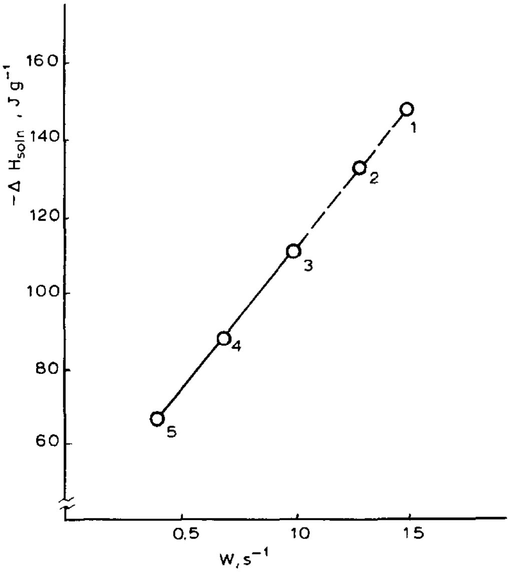

Fig. 2. Interrelation between the enthalpies of solution of cellulose acetates with different degrees of substitution and the velocities of the spin-lattice relaxation of DABO in solutions of DMSO: 1, AC (DS = 0.66); 2, AC (DS = 1.00); 3, AC (DS = 1.66); 4, DAC; 5, TAC.

The results of the thermochemical measurements agree with data on the rotational mobility of molecular NMR relaxation probes [11]. 1,2-Diazobicyclo-2,2,2-octane (DABO) was used in this work as an active probe able to compete with solvent in the formation of hydrogen bonds with the cellulose acetate macromolecules. A linear increase in the velocity of spin-lattice relaxation (W) with decreasing degree of substitution was found for DABO; this testifies to the limitation of its rotational mobility due to the formation of hydrogen bonds with unsubstituted OH groups of the cellulose acetates. The $W = f(DS)$ dependence, like the $\Delta H^0_{soln} = f(DS)$ relationship, is proof of the formation of H-complexes and of the strengthening of the specific intermolecular interactions of polymer with solvent with the decreasing degree of substitution (DS). The interrelation between the thermochemical and microdynamic properties of the cellulose acetate solutions in DMSO is illustrated by the linear correlation between ΔH^0_{soln} and W (Fig. 2).

The given experimental data on the enthalpies of solution allow us to consider the relationships between the influence of the nature and composition of solvents on ΔH^0_{soln} of the cellulose acetates with definite degrees of substitution.

The introduction of chlorinated hydrocarbon additives into trifluoroacetic acid results in an increase in the solvency of mixtures relative to cellulose and its acetates, which is accompanied by the rise in the absolute ΔH^0_{soln} values over the series. $CF_3COOH < CF_3COOH + CHCl_3 < CF_3COOH +$

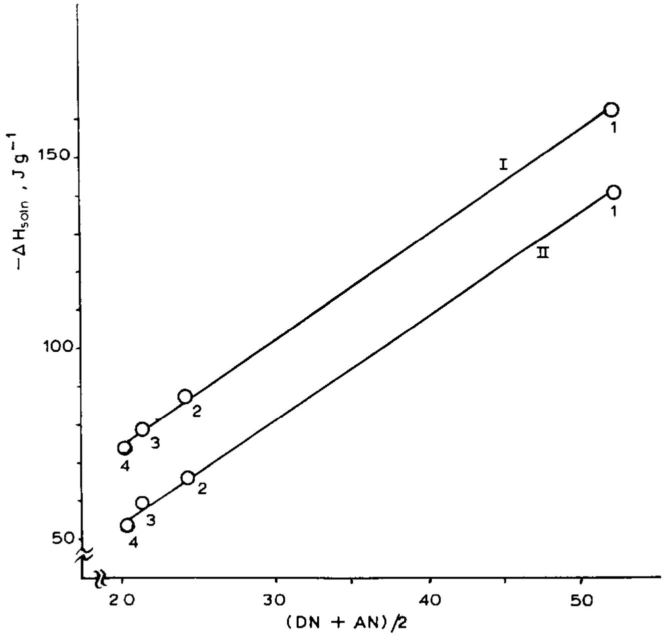

Fig. 3. Dependences of the integral enthalpies of solution of DAC (I) and TAC (II) on the half-sum of the donor and acceptor numbers of individual solvents at 298.15 K: 1, CF_3COOH; 2, DMSO; 3, DMFA; 4, DMAA.

$CH_2Cl_2 < CF_3COOH + C_2H_4Cl_2$. This fact can be explained from the viewpoint of the influence of the chlorinated hydrocarbons on the self-association of the acid and the formation of reactive monomers which, in turn, increases the acceptor properties of the mixtures based on CF_3COOH with respect to polymers.

The increase in the exothermicity of a solution of cellulose acetate is observed over the series DMAA < DMFA < DMSO < CF_3COOH. It is known from NMR spectroscopy data [12] that solvation of cellulose triacetate is executed mainly by way of the interaction of solvent molecules with *O*-acetyl groups and depends on the acceptor properties of solvents. The role of the interaction with the hydroxyl groups which are of a bifunctional nature increases with decreasing degree of substitution. The half-sum of the donor and acceptor numbers was used as a criterion of the EDA ability of the solvent with respect to the cellulose and its esters. Figure 3 shows the linear dependences of ΔH^0_{soln} of DAC and TAC on the $(AN + DN)/2$ values for the solvents studied. It is noteworthy that the linear correlation of ΔH^0_{soln} with the donor–acceptor numbers allows us to unite the experimental results on ΔH^0_{soln} of AC in solvents of different natures which differ substantially with respect to their donor and acceptor properties, from proton-donating CF_3COOH to dipolar aprotic DMAA, DMFA and DMSO.

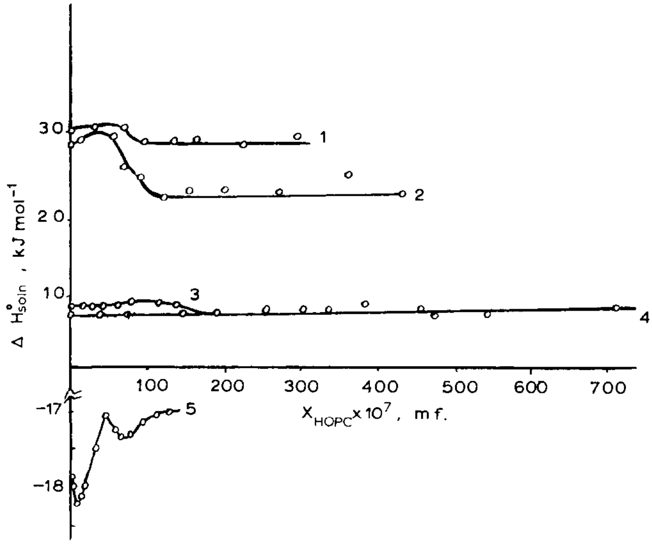

Fig. 4. Dependences of ΔH^0_{soln} of DMSO in HOPC solutions in ethanol (1), DO (2), DMAA (3), DMFA (4) and water (5) on HOPC mole fraction.

Determination of the enthalpies of solution of the cellulose ethers by a direct calorimetric method is experimentally difficult due to the considerable duration of the solution process. It seems reasonable to use the technique based on the introduction of the third component [a liquid low-molecular non-electrolyte (DMSO in our case)] into the polymer–solvent system for evaluation of the thermochemical parameters of the solvation of HOPC and other cellulose ethers. Such a technique of the introduction of non-electrolytes as "probes" is fruitful when studying the processes of solvation in solutions [13].

Figure 4 shows the dependences of the ΔH^0_{soln} of DMSO on the HOPC concentration in water, ethanol, DMAA, DMFA and DO. It can be seen from Fig. 4 that the HOPC concentration does not noticeably influence the values of ΔH^0_{soln} of DMSO in the HOPC–DMAA and HOPC–DMFA systems. At the same time, the influence of the HOPC concentration on the enthalpy of solution of DMSO in water and non-aqueous solvents (DO and ethanol) is clearly manifested. The values of the enthalpies of solution of DMSO in aqueous solutions of HOPC are referred to the exo region, and in non-aqueous solvents to the endo region. It is known that, at concentrations of cellulose and its derivatives in solution greater that 1 wt.%, there is an interaction between polymer molecules to form a fluctuation net of hydrogen bonds [14]. In our case, this is manifested in the HOPC concentration region in solution, $X > 1.2 \times 10^{-5}$ m.f., in which ΔH^0_{soln} values of DMSO do not depend on the concentration of the cellulose ether.

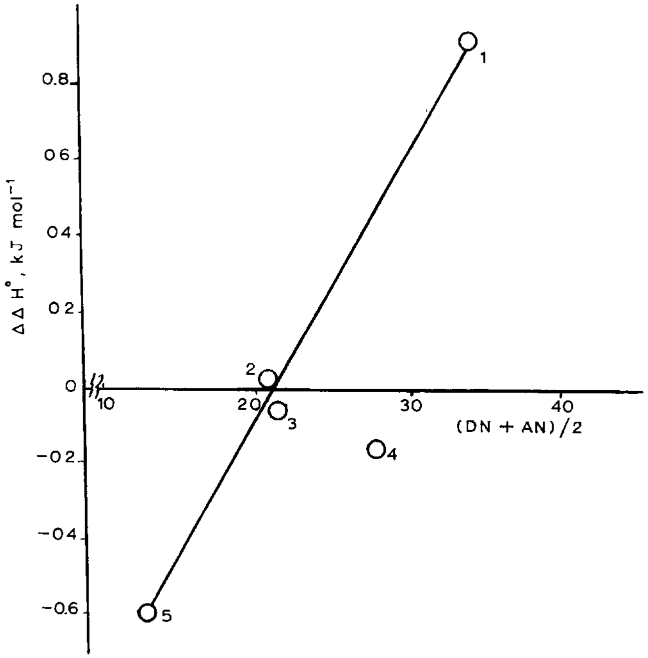

Fig. 5. Enthalpies of transfer, $\Delta\Delta H^0$, of DMSO from solvent to concentrated HOPC solution vs. the donor–acceptor properties of solvents: 1, water; 2, DMAA, 3, DMFA, 4, ethanol, 5, DO.

We used the enthalpies of transfer, ΔH^0_{tr}, of DMSO from individual solvents to concentrated HOPC solution as a thermochemical characteristic sensible to the processes of solvation of polymer in solution. In this case it appeared possible to apply the concept of the determining influence of the donor–acceptor properties of solvents on the thermochemical parameters of the process of HOPC solution. Figure 5 shows the dependence of ΔH^0_{tr} of DMSO on (AN + DN)/2 of solvents. On the whole, a satisfactory linear dependence $\Delta H^0_{\mathrm{tr}} = \mathrm{f(DAN)}$ is observed. An increase in the exothermicity of ΔH^0_{tr} of DMSO is observed with the increase in the values of the half-sum of donor and acceptor numbers; this characterizes the strengthening of the specific solvation of the cellulose ether in this direction.

It should be noted in this connection that a linear correlation between the critical concentration of isotropic–anisotropic phase transition C^* of HOPC in solution and the (AN + DN)/2 of solvents was discovered by us on the basis of experimental data on solubility (Fig. 6). This dependence testifies to the significance of the EDA properties of solvents on formation of the lyotropic liquid-crystalline state of HOPC in solutions. C^* and ΔH^0_{tr} are very important thermodynamic parameters of the solvation of cellulose derivatives in solution.

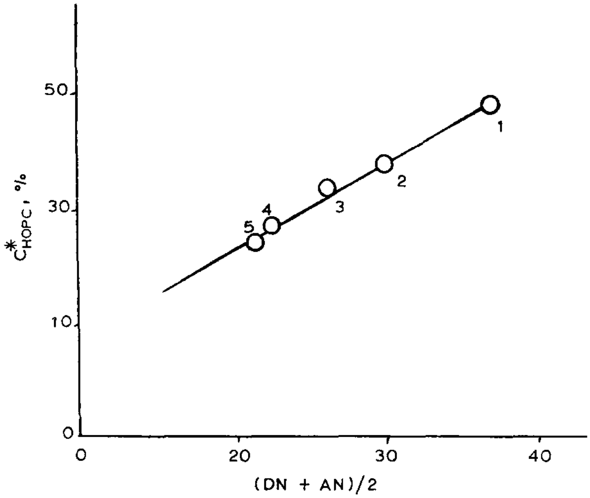

Fig. 6. Dependence of critical concentration, C^*, of HOPC on the half-sum of the donor and acceptor numbers of solvents: 1, water; 2, ethanol; 3, pyridine; 4, DMAA; 5, *N*-methylpyrrolidone.

Thus, the given experimental material on the thermochemical characteristics of non-aqueous solutions of cellulose ethers and esters presents a new universal approach to the quantitative evaluation of the thermodynamic parameters of the processes of specific solvation on the basis of accounting for the EDA ability of polymer and solvent.

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