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# Thermochemistry of the dissolution and characteristics of the solvation of cellulose, polysaccharides, and their derivatives

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ABSTRACT. The results of thermochemical studies on solutions of cellulose, its derivatives, and other polysaccharides are surveyed and treated systematically. The existing ideas about the energy effects due to the amorphous-crystalline structure of polysaccharides, including cellulose, are analysed. It is shown that the enthalpies of solution under the conditions of thermodynamic equilibrium are thermodynamically most preferred. Attention is concentrated on the establishment of a relation between the heats of solution and the electron-donating capacities of the solvent and the polymer. New approaches to the quantitative estimation of the thermochemical parameters of solvation processes in solutions of cellulose and its ethers and esters, based on multiparameter correlations of the enthalpies of solution and transfer with the physicochemical properties of the solvents, are described.

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## I. Introduction

By virtue of their universality, thermochemical methods are widely used in the study of the solvation, dissolution, and interactions of cellulose and its derivatives in solutions.[1–5] The concept of electron donor–acceptor (EDA) complex formation is nowadays of fundamental significance, explaining the nature of the interaction of various organic solvent systems with polysaccharides.[6–8] According to this concept, the energy relations of the EDA interaction in the solution are determined by the electron-donating and electron-accepting capacities of the corresponding centres of the polymer and solvent molecules. The calorimetric method for the study of the specific solvation of cellulose and its derivatives in solutions therefore helps in the development of criteria for the solvent power of non-aqueous solvents on the basis of correlations between the enthalpies of solution and the EDA properties of the liquids.

There exist numerous data for the heats of wetting, swelling, and interaction of cellulose with various liquids, but the question of the elucidation of the relation between the enthalpies of reaction and the EDA capacities of the solvents were considered in only a few studies.[9–11] In our view, no account was taken of the following factors in these investigations.

The data on the heats of reaction of cellulose and its derivatives with solvents refer to non-equilibrium processes occurring in a heterogeneous medium.[1,42] The interpretation of such experimental data is difficult as a consequence of their thermodynamic indefiniteness. Enthalpy of solution data characterising the energy relations of the dissolution process at the molecular level, are best.

In the discussion of experimental results, use was made in the above investigations[9,10] of ether the electron-donating or the electron-accepting capacities of the solvents. The amphoteric nature of the functional groups of cellulose and its derivatives needs to be taken into account when the electron-donating and the electron-accepting properties of liquids are considered jointly.

There are few literature data on the heats of solution of polysaccharides, so that further investigations in the field of the calorimetry of solution of cellulose and its derivatives are essential.

## II. Thermochemistry of the wetting, swelling, and interaction of cellulose with individual solvents, electrolyte solutions, and ionic complexes

Numerous studies have been devoted to the thermochemistry of the interaction of cellulose with liquids and solutions of electrolytes and complexes.[9–11,13–41] A considerable proportion of these studies dealt with the investigation of the heats of wetting, swelling, sorption, and interaction of cellulose with water.[12,13–28]

As a hydrophilic polymer, cellulose exhibits an enhanced affinity for water. However, water molecules are sorbed only by amorphous regions without the disruption of the crystalline regions of cellulose.[9,13] Consequently the enthalpies of reaction with water to a certain extent characterise the ratio of the crystalline and amorphous regions of cellulose, which depend on the previous history of the specimen and the methods of processing and preparation. The integral heats of reaction of the amorphous regions of cellulose with water have been calculated from the ethalpies of reaction of celluloses having different degrees of crystallinity with water.[14,15]

The second decisive factor is the moisture content of the initial specimen. The heats of reaction approach zero for a water content in the specimen corresponding to $P/P_0 \simeq 0.65$. To illustrate this, Fig. 1 presents the variation of the integral enthalpies of reaction with water of specimens of cotton (*1*), wood (*2*), mercerised cotton (*3*), and regenerated (*4*) cellulose and its amorphous regions (*5*) with different moisture contents,[14] the different degrees of crystallinity $X$ of which are respectively 0.70, 0.65, 0.54, and 0.40.

Thermodynamic analysis[14] has shown that, with decrease in the moisture content, the compatibility between the amorphous regions of cellulose and water is determined by the changes in both the enthalpy and entropy of the system. With increase in the water content, the contribution of the enthalpy to the free energy of formation of the system becomes dominant. The appreciable exothermicity of the process is due to the specific interaction between the components with formation of hydrogen bonds.

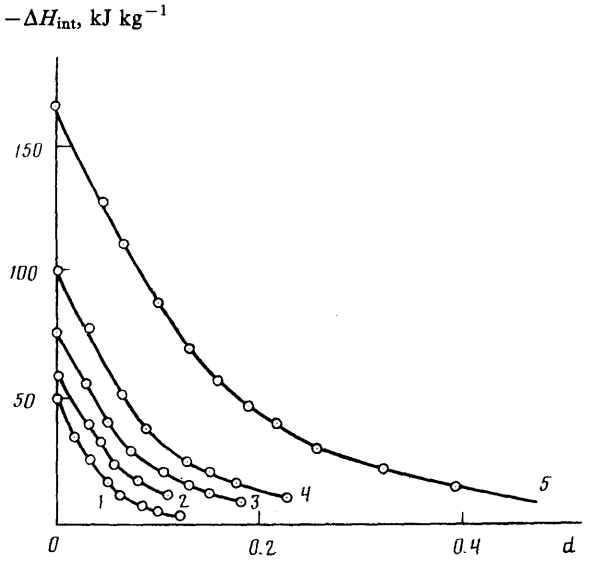



**Figure 1.** Dependence of the integral enthalpies of reaction with water on the water content in the initial specimens: (*1*)–(*5*) see text.

Among the communications devoted to the study of the cellulose–water system, mention should be made of an investigation[21] in which it was assumed that the thermal effects due to three processes contribute to the enthalpy of interaction ($\Delta H_{int}$): the exothermic effect of the solvation of cellulose by water; the endothermic effect of the rupture of the intramolecular and intermolecular hydrogen bonds of cellulose on sorption of water; the exothermic effect of the solvation by water of the free hydroxy-groups formed on dissociation of the hydrogen bonds of cellulose.

The enthalpies of reaction of cellulose with solvents are determined by the nature of the EDA interaction in the systems.[9,10,29–32] As a rule, solvents with inadequate EDA interaction (water, alcohols, nitriles, ethers, and ketones, etc.) mix only with the amorphous component of cellulose. In our view, a general criterion of the solvating capacities of solvents was not put forward in the studies mentioned above.[9,10] Bearing in mind the polyfunctionality of polysaccharides, it is necessary to use jointly the parameters of the electron-donating and electron-accepting properties of the liquids for this purpose. The enthalpies of reaction of wood cellulose with individual liquids are listed in Table 1. The sharp increase in the absolute values of $\Delta H_{int}$ for certain primary amines and strong acids indicates the disruption of the crystalline regions of cellulose and of the specific solvation in the system. However, analysis of the data in Table 1 shows that there is no correlation between the absolute values of $\Delta H_{int}$ and the electron-donating properties of amines. Despite the high electron-donating capacity characteristic of bases such as piperidine ($DN$ = 60.9), diethylamine ($DN$ = 56.1), and triethylamine ($DN$ = 60.1), they are characterised by low enthalpies of reaction with cellulose.

**Table 1.** Enthalpies of the interaction ($-\Delta H_{int}$) of wood cellulose with solvents and empirical parameters of the solvent polarities.

| Solvent | $-\Delta H_{int}$, kJ mol$^{-1}$ | | $DN$ | $AN$ | $\frac{DN+AN}{2}$ |
|---|---|---|---|---|---|
| | 1 : 25 | 1 : 10 | | | |
| Water | 9.6 | 9.2 | 18.0 | 54.8 | 36.4 |
| Methanol | – | 5.0 | 19.0 | 41.3 | 30.15 |
| *N*-Methylformamide | 11.1 | 11.3 | 24.6 * | 31.1 * | 28.35 |
| Dimethylformamide | 10.1 | 10.0 | 26.6 | 16.0 | 21.3 |
| Dimethyl sulphoxide | 13.5 | 13.4 | 29.8 | 19.3 | 25.55 |
| Piperidine | 1.80 | 1.7 | 60.9 * | – | |
| Pyridine | 2.71 | – | 33.1 | 14.2 | 23.65 |
| Diethylamine | 2.51 | – | 56.1 * | 9.4 * | |
| Morpholine | 3.72 | – | | | |
| Tetramethylurea | 1.55 | – | 29.6 | | |
| Triethylamine | 1.35 | – | 60.1 * | 1.4 * | |
| Monoethanolamine | 15.5 | 15.5 | | | |
| Butylamine | 24.3 | – | 47.0 * | – | |
| Hexamethylenediamine (318 K) | 39.4 | – | | | |
| Diethylenetriamine | 40.4 | – | | | |
| Ethylene diamine | 42.0 | 41.8 | 55.0 * | 20.9 * | |
| Hydrazine (95 wt.%) | – | 44.3 | | | |
| Acetic acid | – | 5.0 | 12.7 * | 52.9 | |
| $CF_3COOH$ | – | 36.8 | 0 | 105.3 | 52.65 |
| Phosphoric acid (85 wt.%) | – | 19.2 | – | – | |
| Nitric acid | – | 82.8 | – | – | |

Note. The enthalpies of reaction are listed for 1:25 and 1:10 component ratios (by weight).
*Calculation based on the data of Makitra et al.;[33] in the remaining cases, the data quoted by Burger[68] were used.

It has been suggested[34] that, for effective interaction with cellulose, organic solvents should possess a favourable set of polar, basic, and steric properties. Since the available $\Delta H_{int}$ data refer to non-equilibrium conditions, the establishment of a relation between the heat effects and EDA properties of solvents constitutes an insoluble problem. The enthalpy of solution ($\Delta H_{soln}$) data, characterising the specific solvation process at a molecular level, i.e. under conditions ensuring the complete utilisation of the EDA properties of the solvents, are in this sense preferable for the description of the influence of the solvent on the thermal effects.

Calorimetric data for the interaction of cellulose with aqueous solutions of bases, acids, and salts have been published.[10,11,35–39] The EDA capacity of aqueous electrolyte solutions increases with increase in their concentration. At a certain electrolyte concentration, the exothermicity of the interaction increases owing to the disruption of the crystalline regions of the polymer and the solvation of the macromolecules (Figs. 2 and 3).

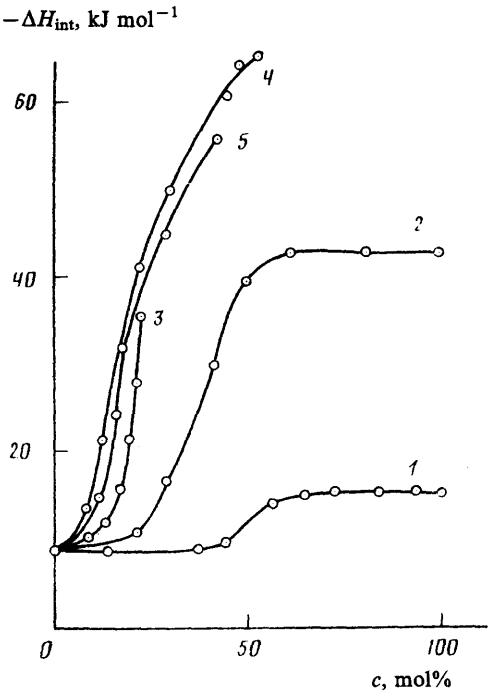



**Figure 2.** Dependence of the enthalpies of reaction of cellulose with aqueous solutions of monoethanolamine (curve *1*), ethylenediamine (curve *2*), and zinc chloride (curve *3*) at 298 K and with sodium hydroxide solutions at 333 K (curve *4*) and 298 K (curve *5*) on the concentrations of the bases and salts.

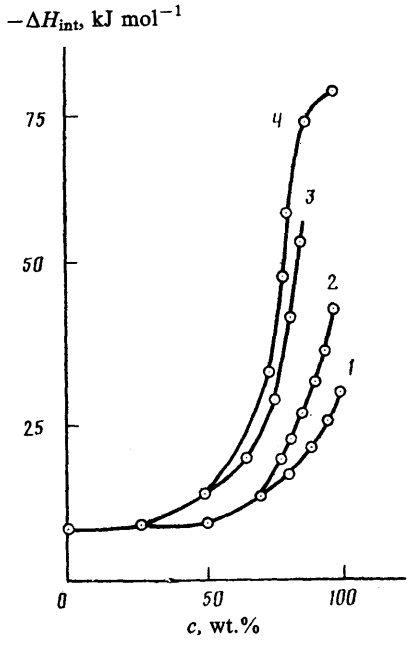



**Figure 3.** Dependence of the enthalpies of reaction of wood cellulose with aqueous solutions of trifluoroacetic (curve *1*), phosphoric (curve 2), sulphuric (curve *3*), and nitric (curve *4*) acids at 298 K on the acid concentration.

We may note that the interaction of cellulose with reactive compounds in solutions leads to the formation of cellulose derivatives. The thermochemical properties of concentrated solutions of metal hydroxides were attributed[11] to the formation of cellulose alkoxides, whilst in other studies[35] they were attributed to inclusion compounds. The interaction of cellulose with strong acid solutions is as a rule accompanied by the formation of the corresponding esters.[40,41] The enthalpies of reaction include additional contributions due to the exchange of the hyroxy-groups for ester groups, the dissolution of the water formed under these conditions in the solution, and the solvation of the product in the solution.

It follows from the data presented that, in a thermochemical study of the swelling, interaction, and dissolution of polysaccharides, it is essential to take into account the additional energy effect associated with the phase state of different regions of the polysaccharides, it is essential to take into account the additional energy effect associated with the phase state of different regions of the polymer.[4,9–11,17,42] The dissolution of polysaccharides having an amorphous-crystalline structure has been represented[42] in the form of three stages. The first involves the transition of the solid polymer to a hypothetical liquid amorphous state, the second is associated with the dissolution and solvation of macromolecules, and the third involves the mixing of the solvated polymer molecules with the solvent to give an infinitely dilute solution. The integral enthalpy of solution $\Delta H_{soln}$ is then regarded as the sum of contributions:

$$\Delta H_{soln} = \Delta H_m + \Delta H_g + \Delta H_{int} + \Delta H_{mix}. \quad (1)$$

The first stage characterises the enthalpy of fusion of crystalline regions ($\Delta H_m$) and the enthalpy of the transition of the amorphous component from the vitreous to the highly elastic ($\Delta H_g$) state. The second entails the interaction ($\Delta H_{int}$) between the polymer and solvent molecules as a consequence of the solvation of the components. The third stage combines all the thermochemical effects of the mixing process ($\Delta H_{mix}$) which occur on dilution (for example, the heats of conformational changes).

Analogous expressions have been proposed[9,10] for the enthalpies of the reactions of cellulose with solvents:

for systems in which the crystalline regions are not disrupted:

$$\Delta H_{int} = \Delta H_g N_a + \Delta H_{mix} N_a; \quad (2)$$

for systems in which the crystalline regions are disrupted:

$$\Delta H_{int} = \Delta H_m N_c + \Delta H_{mix}, \quad (3)$$

where $N_c$ and $N_a$ are the contents of the crystalline and amorphous (vitreous) cellulose (in mole fractions).

The quantities $\Delta H_g$, characterising the transition of the vitreous component of the polysaccharide to the highly elastic state under the influence of the solvent, are particularly large for natural polar polymers with a high glass point $T_g$ ($T_g$ = 493 K for cellulose[13]). Thus, according to Tsvetkov et al.,[10] $\Delta H_g = -12.6 \pm 8$ kJ mol$^{-1}$ unit$^{-1}$ or $-77.5$ J g$^{-1}$ for the fully amorphous vitreous cellulose.

The enthalpy of fusion of the crystalline regions of cellulose can be estimated in different ways. It has been suggested[10] that $\Delta H_m$ be estimated from the enthalpies of solution of laevoglucosan (a compound modelling cellulose) over a wide concentration range. It is assumed that the enthalpy of fusion of crystalline regions of

cellulose is equal to the hypothetical enthalpy of fusion of laevoglucosan and amounts to 14.2 kJ $mol^{-1}$ or 87.3 J $g^{-1}$.

We believe that the most reliable values of $\Delta H_m$ have been obtained from measurements of the enthalpies of solution of cellulose specimens in different solvents.[43,44] The following relation has been used[43] in the determination of the degree of crystallinity:

$$\Delta H_{soln} = -X(\Delta H_c) + + \Delta H_a, \quad (4)$$

where $X$ is the fraction of the crystalline phase in the specimen, $\Delta H_c$ the enthalpy of crystallisation, and $\Delta H_a$ the enthalpy of solution of the amorphous cellulose. In the calculation of $\Delta H_c$, the degrees of crystallinity obtained by X-ray diffraction were used. $\Delta H_c$ is $-15.6$ kJ $mol^{-1}$ ($-96$ J $g^{-1}$) for cellulose (I) and $-19.2$ kJ $mol^{-1}$ ($-118$ J $g^{-1}$) for cellulose (II).

The enthalpy of fusion $\Delta H_m$ for cellulose crystallites has been calculated[44] from the equation

$$\Delta H_m = \Delta H_{inta}(\Delta H_{soln1} - \Delta H_{soln2})/(\Delta H_{int2} - \Delta H_{int1}), \quad (5)$$

where $\Delta H_{int\,a}$ is the enthalpy of reaction with water of the amorphous regions of cellulose, amounting to $-168$ J/g of cellulose at 298 K,[15] $\Delta H_{soln\,1}$ and $\Delta H_{soln\,2}$ are the enthalpies of solution of two cellulose specimens comprising the same crystalline modification, and $\Delta H_{int\,1}$ and $\Delta H_{int\,2}$ are the enthalpies of reaction with water of the same specimens. The quantity $\Delta H_m$ was found to be 36.4 kJ $mol^{-1}$ (224 J $g^{-1}$) for cellulose (I) crystallites and 45.0 kJ $mol^{-1}$ (277 J $g^{-1}$) for cellulose (II) crystallites. These results indicate a greater energetic stability of the cellulose (II) crystallites compared with cellulose (I) crystallites.

Various approaches have been used[10,43,44] for the estimation of the enthalpies of fusion of the crystalline regions of cellulose. However, it is noteworthy that the absence of systematic studies and the necessity to take into account the type of crystalline modification of the polymer preclude at the present time an unambiguous solution of the problem of the reliability of the available literature values of $\Delta H_m$.

We therefore believe that it is essential to pose the problem of the determination of a common standard state in comparing thermodynamic data for processes involving the dissolution and solvation of cellulose and its derivatives. Since the polysaccharides are involatile, the use of an ideal gas as the standard state is excluded. The pure polymers, having an amorphous-crystalline structure, are also unsuitable for this purpose, because it has been shown that the phase state of the polymer plays an important role in the dissolution process. The lack of reliable thermodynamic data for the devitrification and fusion of the polysaccharides precludes an unambiguous solution of this problem. However, bearing in mind that the contributions of $\Delta H_g$ and $\Delta H_m$ have different signs in the range of degrees of crystallinity 0.5–0.7, cancelling out to an appreciable extent, the enthalpies of solution of such specimens of cellulose and its derivatives characterise mainly the specific solvation of the polymer.

The results of the estimation of the enthalpies of reaction from experimental enthalpies of solution of model oxygen- and hydroxyl-containing cellulose compounds in different solvents are of definite interest.[9,10,45–50]

Table 2 shows that the interaction of the model compounds in electron-donating solvents (ethylenediamine, aqueous NaOH solution) takes place preferentially via hydroxy-groups, while in electron-accepting solvents (acids) it involves mainly ester groups.

It has been established from thermochemical data for solutions of cellulose in the ferric sodium tartrate complex (FeTNa),[43,45,47,51] cadoxen,[46,50] and the copper–ammonia complex[52] that the interaction proceeds via two secondary hydroxy-groups. It is noteworthy that the enthalpies of reaction of cellulose and other hydroxylated compounds with FeTNa and cadoxen calculated per hydroxy-group, are close, amounting to 10.9–12.1 kJ/mol of OH groups.[47,50]

**Table 2. Enthalpies of the interaction ($-\Delta H_{int}$) of cellulose and model compounds with solvents at 298 K (kJ $mol^{-1}$) (1:40 ratio by weight).[9]**

| Compound | NaOH (20 wt.%) (ref. 10) | Ethylene-diamine (ref. 10) | MMO*. $H_2O$ (ref. 9) | FeTNa (ref. 45) | $H_3PO_4$ (83 wt.%) (ref. 10, 48) | $CF_3COOH$ (ref. 48) |
|---|---|---|---|---|---|---|
| Wood cellulose | 25.5 | 41.8 | 24.1 | 22.2 | 19.2 | 36.8 |
| Laevoglucosan | 8.4 | 17.6 | −3.5 | – | 0 | – |
| Methanol | 6.3 | 9.6 | – | 6.3 | 8.8 | 14.6 |
| Ethylene glycol | 11.7 | 19.2 | 12.4 | 9.2 | 12.5 | 22.2 |
| Diethylene glycol | 18.4 | 20.1 | 14.8 | 16.0 | 24.2 | 36.8 |
| Glycerol | 15.9 | 28.2 | 21.4 | 13.0 | 15.9 | 27.2 |
| Triethylene glycol | 24.2 | 21.7 | 12.2 | – | 34.3 | 51.4 |

*Methylmorpholine *N*-oxide monohydrate (353 K).

To a first approximation, the enthalpies of mixing of the highly elastic amorphous cellulose with solvents can be estimated as the sum of the enthalpies of reaction via three hydroxy-groups and two oxygen atoms of cellulose. A common approach to the estimation of the values of $\Delta H_{mix}$ from $\Delta H_{soln}$ for model compounds is based on the hypothesis of the additivity of the intermolecular interactions of the functional groups which do not interact strongly with one another. In the case of cellulose, the mutual influence of the functional groups and the steric features of the macromolecular chain alter appreciably the EDA properties of the acetal oxygen atoms and hydroxy-groups.

It has been suggested that[9] the following assumptions be made in the calculation of $\Delta H_{mix}$. The electron-donating capacity of the oxygen atoms of cellulose is equivalent to that of one oxygen atom of the cellulose ether group in model compounds, while the electron-accepting capacity of the hydroxy-groups of the glucopyranose cellulose unit is equivalent to that of four groups of low-molecular-weight alcohols, for example glycerol and ethanol. The enthalpies of reaction of wood cellulose (degree of crystallinity 0.7) with solutions of sodium hydroxide, EDTA, methylmorpholine *N*-oxide, and phosphoric and trifluoroacetic acids calculated on the basis of such a scheme ($-23.5$, $-33.3$, $-24.6$, $-31.6$, and $-51.0$ kJ $mol^{-1}$ respectively) are close in order of magnitude to the values calculated by Eqn. (3) ($-19.9$, $-36.2$, $-18.5$, $-13.6$, and $-31.2$ kJ $mol^{-1}$ respectively). For acids, the values of $\Delta H_{int}$ exceed significantly the experimental values in terms of absolute magnitude. Evidently the approach examined is promising for the qualitative estimation of the enthalpies of reaction of cellulose in solvents of different chemical types. However, more rigorous quantitative calculations require the

development of fundamentally new approaches taking into account all the characteristic features of the intermolecular interactions of both model compounds and of the functional groups in polysaccharide molecules.

When the interaction is of the electron donor–acceptor type, it is essential to take into account the EDA properties of all the system components.[12] Thus the influence of the EDA capacity of the functional groups of the polysaccharide molecules on the solvating capacity of the polymer can be followed by comparing the enthalpies of reaction of cellulose, chitin, and chitosan[53] with organic solvents. The replacement of hydroxy-groups by electron-donating groups (the acetamide group in chitin and the amino-group in chitosan) diminishes the aboslute values of $\Delta H_{int}$ in solutions of bases and increases them in solutions of acids. It has been established on the basis of thermochemical data[9] that the electron-donating capacity of the functional groups of cellulose derivatives in solutions diminishes in the sequence chitosan > chitin > cellulose diacetate > nitrocellulose > monocarboxycellulose.

Thus the following conclusions can be drawn from the analysis of thermochemical data for the enthalpies of reaction (wetting, swelling). In the interpretation of the values of $\Delta H_{int}$, it is essential to take into account the structural features of various regions of the polymer, the previous history of the specimen, and the presence of impurities. The absolute values of $\Delta H_{int}$ for cellulose and its derivatives in solutions are determined by the EDA capacity of the functional groups of the polymer and the solvent. However, the establishment of a relationship between $\Delta H_{int}$ and the EDA properties of solvents is possible only at a qualitative level. For a successful solution of this problem on a quantitative basis, it is necessry to accumulate systematic data for the enthalpies of solution of cellulose and other polysaccharides in non-aqueous solvents.

## III. Thermochemistry of the dissolution and characteristic features of the solvation of cellulose, other polysaccharides, and their derivatives in solutions

The experimental data available at present for the thermochemical properties of solutions of polysaccharides refer mainly to the enthalpies of solution of dextrans,[42,54,55] certain cellulose derivatives (nitrocellulose, cellulose acetates),[56–58] cellulose in solutions of ionic ferric sodium tartrate and cadmium-ethylenediamine (cadoxen) complexes, etc.[43–46,50,51]

Depending on the conditions of their preparation, dextrans undergo structural changes. The experimental densities and heats of solution of dextrans in water and 10% aqueous NaOH solution[54] indicate the polymorphism of polysaccharides.

As in the case of $\Delta H_{int}$ for cellulose materials,[15] a decrease in the absolute magnitude of the enthalpies of solution of dextrans with increase in the degree of crystallinity is observed.

One of the important problems in the thermochemistry of the dissolution of polymers is that of the influence of the molecular weight on the heat change. The enthalpies of solution and dilution of certain low-molecular-weight carbohydrates (saccharides) and dextrans with different molecular weights in water and dimethyl sulphoxide (DMSO) have been determined.[42] The values of $\Delta H_{soln}$ increased with the increase in the molecular weight ($M$) to 1000, while for the fraction with $M$ > 1000 they remained almost unchanged on further increase in $M$. The enthalpies of dilution had the opposite character. The independence of the enthalpies of dilution of the molecular weight for $M$ > 2000 demonstrates very small changes in the helical conformation of dextran and the absence of association in dilute and moderately concentrated solutions.

**Table 3.** The densities and enthalpies of solution of various modifications of dextran.[54]

| Modification | Density of preparation | | $-\Delta H_{soln}$, kJ mol$^{-1}$ | | Degree of crystallinity, % |
|---|---|---|---|---|---|
| | unground | ground | in 10% NaOH | in $H_2O$ | |
| Current state of dextran —amorphous | | | | | |
| – | 1.304 | 1.303 | 44.9 | 29.5 | – |
| Current state of dextran —crystalline | | | | | |
| I | 1.372 | – | 37.5 | 27.2 | 15.0 |
| I | 1.536 | 1.341 | 34.5 | 9.76 | 28.6 |
| II | 1.473 | 1.360 | 39.6 | – | 23.2 |

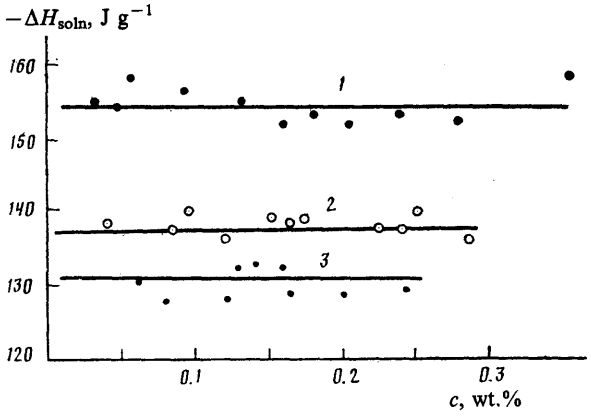



**Figure 4.** Dependence of the enthalpies of solution of dextran with $M$ = 110000 in DMSO (*1*), water (*2*), and formamide (*3*) on the dextran concentration at 298.15 K.

We measured experimentally the integral enthalpies of solution of dextrans with $M = 2 \times 10^4$, $4 \times 10^4$, $7 \times 10^4$, and $11 \times 10^4$ in water, formamide (FA), DMSO, and their mixtures at 298.15 K.

It was found that an increase in the degree of polymerisation (DP) of dextrans from 100 to 680 does not lead to a significant alteration of $\Delta H_{soln}$. This agrees with the theoretical idea that the degree of polymerisation (for specimens with DP > 10) has an insignificant influence on $\Delta H_{soln}$ for flexible-chain amorphous polymers.

Fig. 4 presents the variation of $\Delta H_{soln}$ for dextran with $M$ = 110000 in individual solvents.[55]

At least three processes can contribute to the enthalpy of solution of fully amorphous dextran in a liquid:

$$\Delta H_{soln} = \Delta H_g + \Delta H_{conf} + \Delta H_{soln}. \quad (6)$$

The first ($\Delta H_g$) is the transition of the amorphous polymer from the vitreous to the highly elastic state in solution. $\Delta H_g$ for amorphous dextran is 11.7 kJ mol$^{-1}$ or 72.1 J g$^{-1}$.[10] The second ($\Delta H_{conf}$) involves conformational transformations of the polysaccharide molecules in solution. Since the conformers of dextran in solutions have the same energies,[59] the quantity $\Delta H_{conf}$ can be assumed equal to zero. The third ($\Delta H_{solv}$) is the solvation of a hypothetical liquid dextran by the solvent and is determined by the intermolecular interactions between the solution components. The presence of a multiplicity of hydroxy-groups in the dextran molecule leads to the formation of a stable solvation shell via polymer–solvent hydrogen bonds. The specific features of the solvation are responsible for the large negative values of $\Delta H_{solv}$ (from −54.8 J g$^{-1}$ in formamide to −82.1 J g$^{-1}$ in DMSO).

The exothermicity of the solvation of dextran increases in the sequence formamide ⩽ water < dimethyl sulphoxide. The values of $\Delta H_{solv}$ in formamide and water are close in absolute magnitude, which is apparently due to the characteristics of the individual solvents. The need to take into account both electron-donating and electron-accepting properties of the liquids in the solvation of a polysaccharide arises from the bifunctional nature of the hydroxy-groups of dextran. It has been suggested[60] that half the sum of their *DN* and *AN* numbers be used as a criterion of the donor–acceptor capacity of the solvent. Formamide and water are characterised by similar values of (*DN* + *AN*)/2—31.9 and 36.4 respectively. Furthermore, formamide and water are highly associated liquids with similar FA–FA, water–water, and FA–water hydrogen bond energies (~15.5 kJ mol$^{-1}$).[61]

The greater exothermicity of the solvation of dextran in DMSO compared with water and formamide is due to the complex influence of a set of factors. Thus the Flory parameter of the dextran–DMSO interaction is an order of magnitude higher than for the dextran–water interaction,[42] while according to $^{13}$C NMR data[62] the conformational mobility of dextran micromolecules in water is greater than in DMSO. The endothermic contribution to $\Delta H_{solv}$ associated with the rupture of the solvent–solvent bonds is smallest in DMSO among all the liquids investigated.

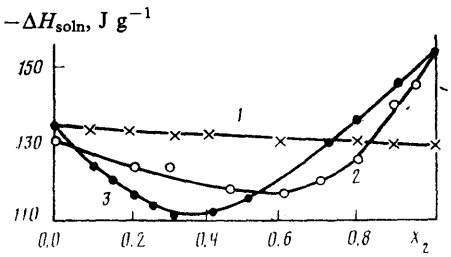



**Figure 5.** Enthalpies of solution of dextran with $M$ = 110000 in water–formamide (curve *1*), formamide–DMSO (curve *2*), and water–DMSO (curve 3) mixtures at 298.15 K ($X_2$ = mole fraction of the second mixture component).

Fig. 5 presents the dependence of the integral enthalpies of solution of dextran with $M$ = 110000 in water–formamide, water–DMSO, and formamide–DMSO mixtures on the composition of the mixed solvent at 298.15 K. The nature of the dependences of $\Delta H^\circ_{soln}$ on the mixed solvent composition is various. The dependence of $\Delta H^\circ_{soln}$ for dextran on the composition of the water–formamide mixture is linear. The water–DMSO and formamide–DMSO systems are characterised by an extremum in the $\Delta H^\circ_{soln} = f(X)$ relation. The nature of the observed dependences of $\Delta H^\circ_{soln}$ for the polysaccharide on the solvent composition is associated with the characteristic features of the donor–acceptor interaction between the mixture components. In the range of compositions where an exothermic minimum is observed in $\Delta H^\circ_{soln}$, the molecular interaction of the solvent components is strongest. This confirms the similarity of the variations of the enthalpies of solution of dextran in solvent mixtures and of the enthalpies of mixing of the components of the binary solvent.[61] The formation of mixed associated species comprising the molecules of low-molecular-weight substances over the entire range of compositions weakens the solvation of dextrans and hence diminishes the exothermicity of the dissolution process.

Fig. 6 presents the dependences of the enthalpies of transfer of dextran from DMSO in water–DMSO and formamide–DMSO mixtures on the DMSO mole fraction, which characterise the enthalpy component of the solvation of dextran in the systems investigated. The figure shows that the dependence of $\Delta H^\circ_{trans}$ for the water–DMSO system is characterised by a concavity on the descending section of the extremum for $X_{DMSO}$ > 0.5 (mole fraction). The similar form of the relations for solutions of low-molecular-weight saccharides and polyhydric alcohols indicates the occurrence of selective solvation.[63] In the present instance, this implies that the hydroxy-groups of dextran are selectively solvated by water in the water–DMSO mixture. This conclusion agrees with those of an investigation[64] whose authors demonstrated the occurrence of the selective solvation of dextrans in a water–DMSO mixed solvent by gel-permeation chromatography.

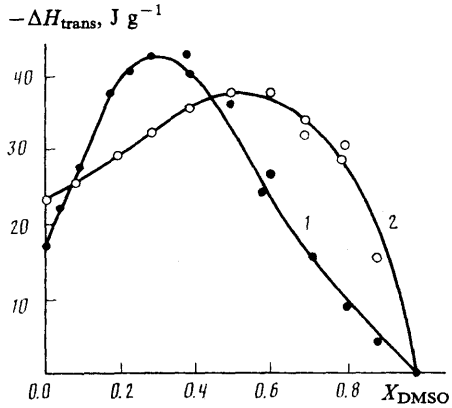



**Figure 6.** Enthalpies of transfer of dextran from DMSO in water–DMSO (curve *1*) and formamide–DMSO (curve *2*) mixtures at 298.15 K.

Comparison of the $\Delta H^\circ_{trans} = f(X)$ relations shows that, in contrast to the water–DMSO system, in the non-aqueous formamide–DMSO mixed solvent there is no selective solvation of the macromolecules. This is due to the difference between the

mechanisms of the formation of hydrogen bonds in the aqueous organic and composite non-aqueous solvents with dextran macromolecules.

Fig. 7 presents the dependences of the enthalpies of solution of cellulose (C), cellulose acetate (CA), cellulose diacetate (CDA), and cellulose triacetate (CTA) on the degree of substitution $\gamma$ of the hydroxy-groups by acetate groups in non-aqueous individual and mixed solvents at 298.15 K. Evidently, for all the solvents investigated, there is a linear relation between the enthalpies of solution and the amount of bound acetic acid in cellulose acetates. The increase in the exothermicity of the dissolution of cellulose acetates in non-aqueous solvents with decrease in the degree of substitution is caused by the increased EDA capacity of the polymers.

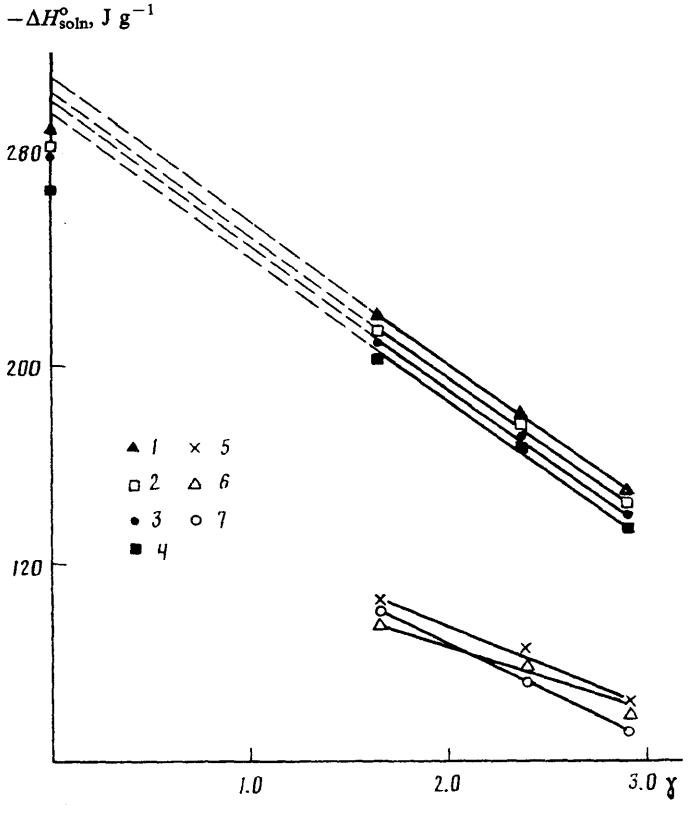



**Figure 7.** Dependence of the integral enthalpies of solution of cellulose, cellulose acetate, cellulose diacetate, and cellulose triacetate on the degree of substitution of hydroxy-groups by acetate groups in different solvents at 298.15 K: *1*, $CF_3COOH + C_2H_4Cl_2$; *2*, $CF_3COOH + CH_2Cl_2$; *3*, $CF_3COOH + CHCl_3$; *4*, $CF_3COOH$; *5*, DMSO; *6*, DMF; *7*, DMA.

In a thermochemical study of the dissolution of cellulose and its derivatives, it is essential to take into account the energy contributions associated with the fusion of the crystalline regions of the polymers ($\Delta H_m$) and the transition of their vitreous regions to the highly elastic state under the influence of solvents ($\Delta H_g$). The quantities $\Delta H_m$ and $\Delta H_g$ for cellulose are respectively 13.4 and 12.6 kJ mol$^{-1}$ unit$^{-1}$,[10] i.e. in the case of specimens with a degree of crystallinity of 0.59 the contributions of $\Delta H_m$ and $\Delta H_g$ to a large extent cancel out. In our view, the foregoing consideration can be applied also to cellulose acetate specimens. Thus the values of $\Delta H^{\circ}_{soln}$ characterise mainly the specific solvation of the polymers and their absolute values are determined by the donor–acceptor properties of the solution components.

The results of the thermochemical measurements agree with data for the rotational mobility of molecular NMR-relaxation probes.[65] 1,4-Diazabicyclo[2.2.2]octane (DABO) was used in the present study as an active probe capable of competing with the solvent for the formation of hydrogen bonds with the molecules of cellulose acetates. A linear increase in the rate of spin–lattice relaxation $W$ accompanied by a decrease in the degree of substitution $\gamma$ has been found for DABO, indicating the restriction of its rotational mobility as a consequence of the formation of hydrogen bonds with the unsubstituted OH groups of cellulose acetates. Like the $\Delta H^{\circ}_{soln} = f(\gamma)$ relation, the $W = f(\gamma)$ relation constitutes proof of the formation of hydrogen-bonded complexes and of the intensification of the specific intermolecular interactions of the polymer with the solvent as the degree of substitution diminishes. The relation between the thermochemical and microdynamic properties of solutions of cellulose acetates in DMSO is illustrated by the linear correlation between $\Delta H^{\circ}_{soln}$ and $W$ (Fig. 8). On extrapolation of the linear relations between $\Delta H^{\circ}_{soln}$ and the degree of substitution to zero values of the latter for solutions of cellulose acetates in trifluoroacetic acid and its mixtures with chlorinated hydrocarbons, the hypothetical enthalpies of solution of cellulose in these solvents were obtained (Fig. 7). The extrapolated and experimental values of $\Delta H^{\circ}_{soln}$ are close in absolute magnitude (the difference is not more than 15 J g$^{-1}$). This is due to the differences between the degrees of crystallinity of specimens of wood cellulose and cellulose acetates.

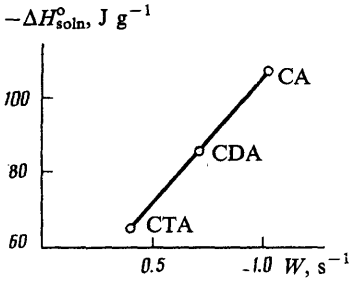



**Figure 8.** Dependence of the integral enthalpies of solution of cellulose acetates with different degrees of substitution on the rate of the spin–lattice relaxation of the $^{13}C$ nuclei in low-molecular-weight probes.

Using the literature values of the heats of fusion of cellulose[10] and the difference between the degrees of crystallinity, we estimated the endothermic contribution to $\Delta H^{\circ}_{soln}$ associated with the fusion of additional regions of cellulose. It proved to be 15 J g$^{-1}$. Thus the validity of the linear extrapolation to the zero degree of substitution

was confirmed and the retention of this type of dependence of $\Delta H^{\circ}_{soln}$ on the latter factor was demonstrated.

The amount of acetic acid bound in cellulose acetates can be determined calorimetrically on the basis of the observed dependence of the heats of solution of cellulose and its acetates in various solvents on the degree of substitution. The experimental data permit a comparative analysis of the influences of the nature and composition of the solvents on $\Delta H^{\circ}_{soln}$ for cellulose acetates with a definite degree of substitution.

The addition of chlorinated hydrocarbons $C_xH_yCl_z$ to trifluoroacetic acid increases the solvent power of the mixtures in relation to cellulose and its acetates,[66] which is accompanied by an increase in the absolute values of $\Delta H^{\circ}_{soln}$ in the sequence $CF_3COOH < CF_3COOH + CHCl_3 < CF_3COOH + CH_2Cl_2 < CF_3COOH + C_2H_4Cl_2$. This fact can be explained by the influence of chlorinated hydrocarbons on the self-association of the acid[67] and the formation of reactive acid monomers, which increases, in turn, the electron-accepting properties of the $CF_3COOH$-based mixtures in relation to the polymers.

In the series of individual solvents, an increase in the exothermicity for cellulose acetates is observed: dimethylacetamide (DMA) < dimethylformaide (DMF) < DMSO < trifluoroacetic acid. On solvation of cellulose and its derivatives, it is essential to take into account the mixed donor–acceptor capacity of the solvents.

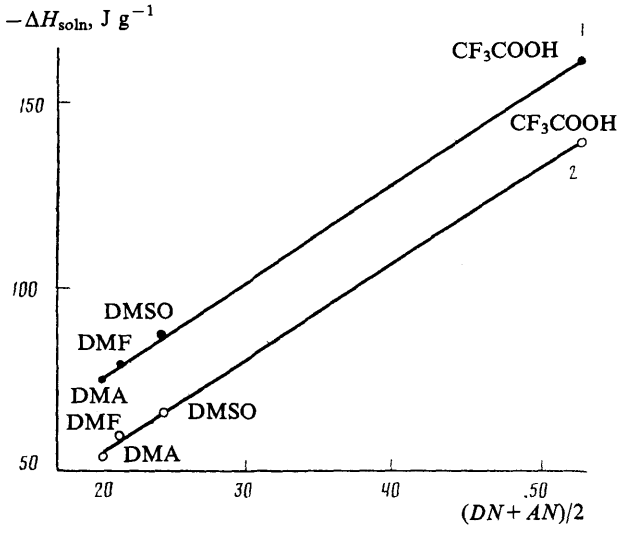



**Figure 9.** Dependence of the integral enthalpies of solution of cellulose diacetate (line *1*) and cellulose triacetate (line *2*) on half the sum of the donor and acceptor numbers of the individual solvents at 298.15 K.

The decisive role of specific solvation in the dissolution of the acetates is confirmed by the linear relation between $\Delta H^{\circ}_{soln}$ for cellulose diacetate and triacetate and half the sum of the donor and acceptor numbers $(DN + AN)/2$ for the solvents investigated (Fig. 9). Such linear correlation makes it possible to combine the result of the determination of $\Delta H^{\circ}_{soln}$ for cellulose acetates in solvents of different nature, differing significantly in their electron-donating and electron-accepting properties—ranging from the proton donating $CF_3COOH$ to the dipolar aprotic solvents DMA, DMF, and DMSO.

We have thus shown that in dilute solutions of cellulose and its derivatives, the donor–acceptor interaction between the components is decisive. On the other hand, one can postulate that in the case of concentrated solutions of the polysaccharides it is not legitimate to relate the thermodynamic characteristics of the dissolution process to any one physicochemical parameter of the solvent. The limitations of simple correlations necessitate the application of more complex models.[68] The choice of a multiparameter model is determined by the type of the process in which particular physicochemical properties of the solvents predominate. Analysis of the available information about the structural-thermodynamic characteristics of solutions of cellulose and its derivatives[3] leads to the conclusion that the enthalpy contribution predominates over the entropy contribution. Processes of this kind are described satisfactorily by the Gutmann–Mayer and Krigovskii–Fossett models.[68] We confirmed the fruitfulness of this approach in a study of concentrated solutions of hydroxypropylcellulose in different solvents.

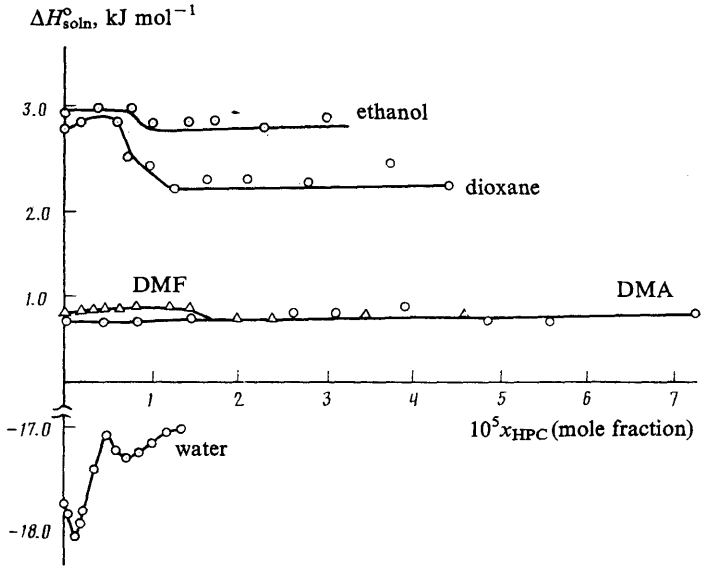



**Figure 10.** Dependence of the integral enthalpies of solution of DMSO in solutions of hydroxypropylcellulose on the mole fraction of hydroxypropylcellulose.

The experimental determination of the enthalpies of solution of cellulose ethers is difficult in view of the long time required for the attainment of equilibrium in dissolution processes. In order to find the thermochemical parameters of the solvation of hydroxypropylcellulose (HPC) and other cellulose ethers, it appears useful to introduce into the binary polymer–solvent system a third component—a liquid non-electrolyte—as a "probe" for solvation processes. Such a methodological procedure is extremely fruitful in the study of solvation processes in liquids.

We determined the enthalpies of solution of DMSO in solutions of hydroxypropylcellulose in water, ethanol, DMA, DMF, and dioxane (DO). The results of the thermochemical studies are presented in Fig. 10. Evidently the concentration of hydroxypropylcellulose does not exert a significant influence on $\Delta H^{\circ}_{soln}$ for DMSO in the HPC–DMA and HPC–DMF systems. On the other hand, the influence of the hydroxypropylcellulose concentration on the enthalpy of solution of DMSO in water and certain non-aqueous solvents (dioxane and ethanol) is clearly manifested. Furthermore, the increase in $\Delta H^{\circ}_{soln}$ for DMSO can be seen in the series of solvents water < DMA < DMF < DO < ethanol.

The enthalpies of solution of DMSO in ethanol, DMA, and DMF were determined for the first time. The enthalpies $\Delta H^{\circ}_{soln}$ for DMSO in water and dioxane agree well with the literature values.[61,69]

The enthalpies of solution of DMSO in aqueous solutions of hydroxypropylcellulose are exothermic, while in non-aqueous solutions they are endothermic. These results can be explained from the standpoint of the donor–acceptor properties of the solvents.

It is known that the mixing of two electron-donating liquids is accompanied by an endothermic effect.[70] A similar effect occurs on mixing DMSO with ethanol. This phenomenon can be accounted for by a change in the electron-donating capacity of ethanol in the associated state, which is indicated by the donor numbers: $DN_{SbCl_5}$ = 18.5,[68] $DN_{bulk}$ = 27.8 according to Marcus,[71] and $DN_{bulk}$ = 32 according to Gutmann.[71]

The first stage in the study of the characteristic features of solvation in the solvent (I)–solvent (II)–polymer systems was the determination of $\Delta H^{\circ}_{soln}$ for DMSO (solvent I) in the individual solvents II. On passing from DMSO–solvent II mixtures to the hydroxypropylcellulose–solvent II systems, the values of $\Delta H^{\circ}_{soln}$ for DMSO change owing to polymer solvation processes in the solution. It is known that,[57] when the concentrations of cellulose and its ethers are greater than 1 wt.%, the polymer molecules interact with formation of a fluctuating network of hydrogen bonds. In our case, this is manifested in the range of hydroxypropylcellulose concentrations in the solutions $X_{HPC} > 125 \times 10^{-7}$ (mole fraction), while the enthalpy of solution of DMSO does not change with increase in the polymer concentration.

The extremum in the $\Delta H^{\circ}_{soln} = f(X_{HPC})$ relation is probably associated with the change in the structure of the solutions. The increase in the exothermicity of the dissolution of DMSO in an aqueous HPC solution for a mole fraction of $7.5 \times 10^{-7}$ is a result of the disruptive effect of polymer molecules on the water structure. A further increase in the hydroxypropylcellulose concentration leads to the stabilisation of the aqueous solutions.[72] In the region of the concentrations corresponding to the second minimum, several factors are superimposed: the simultaneous strengthening of the intermolecular hydrogen bonds between the molecules of the dissolved polymer and the transolvation of the dissolved hyroxypropylcellulose molecules by water molecules induced by this factor. The general trend towards a decrease in the exothermicity of the interaction with DMSO with increase in the hydroxypropylcellulose concentration in the aqueous solution is probably associated with the stabilisation of the structure of the solution as a result of the formation of cooperative HPC–HPC and HPC–water hydrogen bonds.

In non-aqueous solutions for $X_{HPC}$ up to a mole fraction of $125 \times 10^{-7}$, $\Delta H^{\circ}_{soln}$ for DMSO remains constant within the limits of experimental error. Bearing in mind that ethanol, dioxane, DMF, and DMA are associated liquids, one can postulate the retention of the primary structure of the solvent after the introduction of small amounts of added polymer.

The enthalpies of the transfer of the test substance from one solvent to another can be conveniently used as a thermochemical characteristic of the solvation of atomic-molecular species in a series of individual solvents. We used the enthalpies of transfer ($\Delta H^{\circ}_{trans}$) of DMSO from an individual solvent to a concentrated polymer solution as thermochemical characteristics sensitive to solvation processes. Fig. 11 presents the dependence of $\Delta H^{\circ}_{trans}$ on the ratio of the donor and acceptor numbers of the solvents. The relation is non-linear with a minimum in the exothermicity of the enthalpies of transfer of DMSO corresponding to the region of equal donor and acceptor numbers ($DN/AN$ = 1).

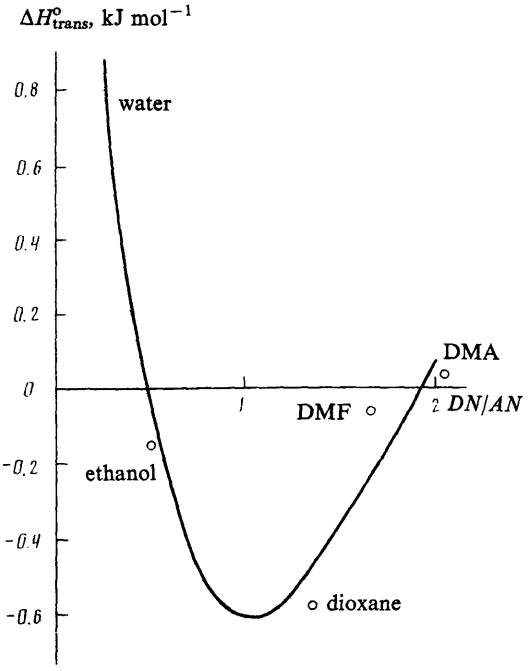



**Figure 11. Dependence of the enthalpies of transfer of DMSO from the individual solvents to concentrated solutions of hydroxypropylcellulose on the ratio of the donor and acceptor numbers of the solvents.**

In order to establish the relation between the phyisochemical properties of the solvents and the experimental thermochemical parameters [$\Delta H^{\circ}_{soln}$ for DMSO, and the enthalpy of the transfer of the latter ($\Delta H^{\circ}_{trans}$) from the solvent to hydroxypropylcellulose solutions], methods of mathematical statistics were employed. The calculations were performed on an EC 1060 computer. The parameters of the solvents for such analysis are presented in Table 4. Pair and multiple regression analyses of $\Delta H^{\circ}_{trans}$, $\Delta H^{\circ}_{trans}/\Delta^{\circ}_{soln}$, and the physicochemical properties of the solvents were carried out.

The results of the calculation of the coefficients of the pair correlation of $\Delta H^{\circ}_{trans}$ and $\Delta H^{\circ}_{trans}/\Delta H^{\circ}_{soln}$, on the one hand, and the properties of the solvents, on the other, are presented in Table 5.

**Table 4.** Physicochemical parameters of the solvents.

| Parameter | Water | Ethanol | DMA | DMF | 1,4-Dioxane | References |
|---|---|---|---|---|---|---|
| $\frac{n^2-1}{n^2+2}$ | 0.2054 | 0.2214 | 0.2647 | 0.2584 | 0.2543 | [33] |
| $\frac{\varepsilon-1}{2\varepsilon+1}$ | 0.490 | 0.470 | 0.480 | 0.480 | 0.223 | [33] |
| $B$, cm$^{-1}$ | – | 235 | 343 | 291 | 237 | [33] |
| $E_T^1$, Kj mol$^{-1}$ | 264.1 | 217.3 | 183.0 | 183.4 | 150.7 | [33] |
| $Z^1$, kJ mol$^{-1}$ | 296.0 | 333.2 | 280.0 | 286.7 | 270.4 | [33] |
| $DN^2_{SbCl_5}$ | 18 | 19.2 | 27.8 | 26.6 | 14.8 | [68, 73] |
| $AN$ | 54.8 | 37.1 | 13.6 | 16.0 | 10.8 | [68, 73] |
| $\pi^*$ | 1.09 | 0.54 | 0.88 | 0.88 | 0.55 | [75] |
| $\varepsilon$ | 78.3 | 25.2 | 37.8 | 36.7 | 2.21 | [75] |
| $\mu(D)$ | 1.84 | 1.69 | 3.81 | 3.86 | 0.4 | [75] |
| $\overline{V}$, cm$^3$ mol$^{-1}$ | 18.07 | 58.69 | 92.98 | 81.12 | 85.71 | |
| $\rho$, g cm$^{-3}$ | 0.997 | 0.785 | 0.937 | 0.901 | 1.028 | [76] |
| $\delta$, J m$^{-3}$ | 98.08 | 54.33 | 46.55 | 50.86 | 41.90 | [76] |

Note. The following parameters of the solvents are listed: the polarisability $(n^2 - 1)/(n^2 + 2)$, the polarity $(\varepsilon - 1)/(2\varepsilon + 1)$, the basicity $B$, the Richardt–Dimroth electrophilicity parameter $E_T$, the Kosower electrophilicity parameter $Z$, the Kamlet–Taft dipolarity parameter $\pi^*$, the dielectric constant $\varepsilon$, the dipole moment $\mu$, the molar volume $\overline{V}$, the density $\rho$, the three-dimensional solubility parameter $\delta$, and the Hildenbrandt parameter.

**Table 5.** Coefficients of the pair correlations of $\Delta H^\circ_{trans}$ and $\Delta H^\circ_{trans}/\Delta H^\circ_{soln}$ with the physicochemical properties of the solvents.

| Solvent parameter | $r\Delta H^\circ_{trans}$ | $r\Delta H^\circ_{trans}/\Delta H^\circ_{soln}$ |
|---|---|---|
| $(DN+AN)/2$ | 0.70 | 0.61 |
| $\delta$ | 0.74 | 0.53 |
| $\overline{V}$ | −0.63 | −0.46 |
| $\mu$ | 0.32 | 0.47 |
| $\varepsilon$ | 0.90 | 0.66 |
| $\pi^*$ | 0.65 | 0.59 |
| $Z$ | 0.68 | 0.52 |
| $E_T$ | 0.71 | 0.59 |

Comparison of the correlations of $\Delta H^\circ_{trans}$ and $\Delta H^\circ_{trans}/\Delta H^\circ_{soln}$ makes evident the advantages of using absolute rather than relative heats of transfer for the estimation of the influence of the solvent. The most significant parameters influencing $\Delta H^\circ_{trans}$ are the dielectric constant, the Hildebrandt parameters, the Richardt–Dimroth electrophilicity parameter, and the sum of the donor and acceptor numbers of the solvents. The regression coefficients decrease in the above series from 0.9 to 0.7. Since there is a high degree of correlation between $\Delta H^\circ_{trans}$ and $\varepsilon$, it is useful to employ a linear regression model of the type

$$\Delta H^\circ_{trans} = A + B\varepsilon, \qquad (7)$$

The coefficients of this model are presented in Table 6.

**Table 6.** Experimental and calculated heats of transfer of DMSO from the solvent to the hydroxypropylcellulose solution (kJ mol$^{-1}$) obtained with the aid of the linear model (7) and by fitting the multiple agreesion equation (8).

| Solvent | $\Delta H^\circ_{trans}$ (experiment) | $\omega H^\circ_{trans}$ [calc. by Eqn. (7)] | $\Delta H^\circ_{trans}$ (expt)− $-\Delta H^\circ_{trans}$ [calc. by Eqn. (7)] | $\Delta H^\circ_{trans}$ [calc. by Eqn. (8)] | $\Delta H^\circ_{trans}$ (expt)− $-\Delta H^\circ_{trans}$ [calc. by Eqn. (8)] |
|---|---|---|---|---|---|
| Water | 0.870 | 0.825 | 0.045 | 0.874 | −0.004 |
| Ethanol | −0.164 | −0.196 | 0.032 | −0.168 | 0.004 |
| DMA | 0.021 | 0.046 | −0.025 | −0.003 | 0.024 |
| DMF | −0.069 | 0.025 | −0.094 | −0.050 | −0.019 |
| 1,4-Dioxane | −0.596 | −0.638 | 0.042 | −0.591 | −0.005 |

Note. The following parameters were adopted in the calculation by Eqn. (7): $A = -0.6809 \pm 0.0669$ and $R = 0.01924 \pm 0.00153$; the following parameters were adopted in the calculation by Eqn. (8): $A_0 = 0.1953 \pm 0.0396$, $A_1 = 0.6517 \pm 0.0446$, $A_2 = 0.7687 \pm 0.2491$, and $A_3 = -0.6753 \pm 0.2517$.

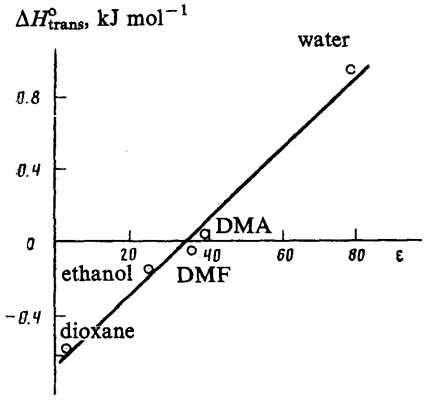



**Figure 12.** Dependence of $\Delta H^\circ_{trans}$ on the dielectric constants of the solvents.

Comparison of the results of the calculation with experimental data shows that the absolute error in the fitting of Eqn. (7) is not more than 0.094 kJ mol$^{-1}$. The criterion of the linear fit $F$, defined as the ratio of the variance of the average value of $\Delta H^\circ_{trans}$ to the variance of the calculated values, is 39.9. It characterises the quality of the proposed model (Fig. 12). Since a decrease in the pair correlation coefficients is observed for other physicochemical parameters (Table 5), they cannot be used to construct a one-parameter linear model similar to that defined by Eqn. (7). In constructing models with the aid of multiple regression, singular analysis of an undefined system of equations,[77] and computer methods, the following best fit was obtained:

$$\Delta H^\circ_{trans} = A_0 + A_1X_1 + A_2X_2 + A_3X_3,$$
$$X_1 = \frac{\varepsilon-40}{38}, \quad X_2 = \frac{E_T-50}{74}, \quad X_3 = \frac{(DN+AN)/2-24}{12}. \qquad (8)$$

The coefficients of this equation, the results of the calculation, and the experimental data are presented in Table 6. The criterion $F$ is 292 and the error of the calculation does not exceed 0.024, which indicates a high accuracy of the multiparameter fit. All the coefficients of Eqn. (8) are significant at a level of fiducial probability exceeding 95% (Fig. 13).

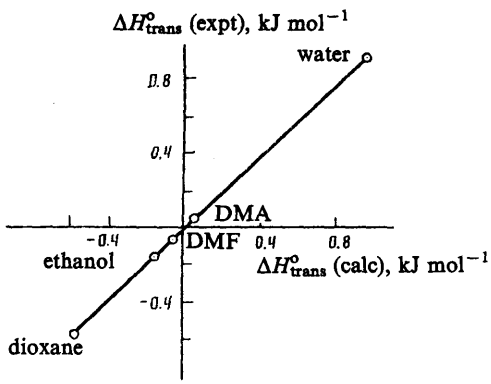



**Figure 13.** Experimental and calculated [by Eqn. (8)] enthalpies of transfer of DMSO from the solvent to the hydroxy propylcellulose solution.

The model developed is analogous to the Krigovskii–Fossett model,[68] which is applicable to the description of the influence of the solvent on the thermodynamics of solvation processes characterised by a significant contribution of the enthalpy factor.

Analysis of the significance of the coefficients of Eqn. (8) shows that the most significant contribution to the enthalpy characteristic of the solvation of DMSO in the hydroxypropylcellulose–solvent I–solvent II system is determined by the dielectric properties of the non-aqueous solvents. This agrees with the data of Solomonov et al.,[78] indicating a significant contribution of non-specific solvation to the enthalpies of solvation of organic non-electrolytes.

The characteristic features of the proposed model are determined by the necessity to take into account the combination of the donor and acceptor numbers of the non-aqueous solvents under the conditions of the specific solvation of the hydroxy-groups in the cellulose macromolecules (which have both electron-donating and electron-accepting properties).

With the aim of further development of the proposed approach to the study of concentrated solutions of cellulose derivatives, we measured the enthalpies of solution of poly(ethylene glycol) (a high-molecular-weight probe) with $M = 400 \pm 20$ in solutions of cellulose acetates with different degrees of substitution in DMSO. The results of the thermochemical measurements are presented in Fig. 14. The dissolution of poly(ethylene glycol) in the test systems is characterised by negative values of $\Delta H^{\circ}_{soln}$. Analysis of the observed concentration variations of the enthalpies of solution reveals their varied character. For solutions of cellulose acetates with $\gamma = 0.63$, there is virtually no dependence of $\Delta H^{\circ}_{soln}$ for poly(ethylene glycol) on the cellulose acetate concentration in solution. In the case of individual cellulose acetates, the exothermicity of the dissolution of poly(ethylene glycol) increases in the range of concentrations from 1 to 2 wt.%, which indicates the occurrence of the poly(ethylene glycol)–cellulose acetate interaction.

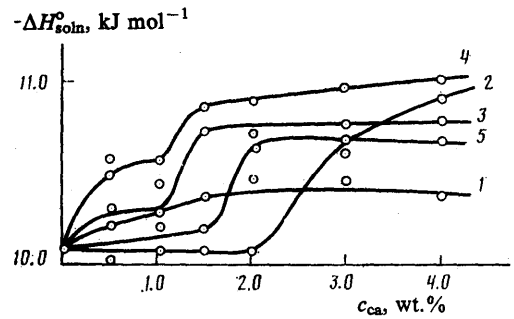



**Figure 14.** Dependence of the enthalpies of solution of poly(ethylene glycol) in solutions of cellulose acetate with different degrees of substitution $\gamma$ in DMSO on the polymer concentration ($c_{CA}$, wt.%): *1*, 0.63; *2*, 0.96; *3*, 1.55; *4*, 2.43; *5*, 2.90.

Fig. 15 illustrates the dependence of the initial concentration at which the absolute values of $\Delta H^{\circ}_{soln}$ for poly(ethylene glycol) increase in solutions of cellulose acetate on the degree of substitution $\gamma$. This dependence clearly illustrates the tendency towards a decrease in $c_{init}$ with increase in $\gamma$ for cellulose acetate, which is apparently due to the formation of a fluctuation network of intramolecular and intermolecular bonds in cellulose acetate.[3]

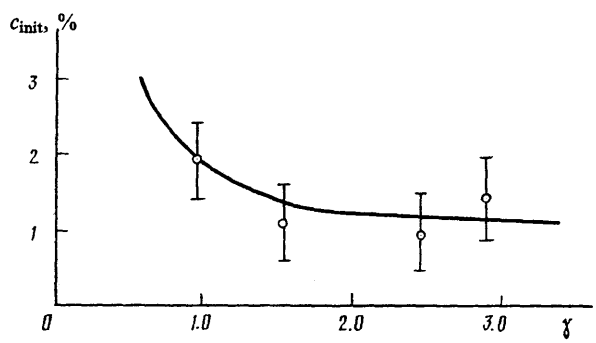



**Figure 15.** Dependence of the initial concentration corresponding to the onset of the change in $\Delta H^{\circ}_{soln}$ for poly(ethylene glycol) in solutions of cellulose acetates on the degree of substitution.

Fig. 16 presents the dependence of the enthalpies of transfer of poly(ethylene glycol) from DMSO to a cellulose acetate solution at the initial concentration $c_{init}$ on the degree of substitution $\gamma$. In the range $0.6 < \gamma < 1.0$, an abrupt increase in the exothermicity of the

transfer process is observed, which is associated with the intensification of the poly(ethylene glycol)–cellulose acetate intermolecular interactions. For $\gamma \geqslant 1.0$, the absolute values of $\Delta H^{\circ}_{trans}$ for poly(ethylene glycol) hardly depend on the degree of substitution. The similarity of the values of $\Delta H^{\circ}_{trans}$ for poly(ethylene glycol) in terms of absolute magnitude in solutions of cellulose acetate indicates the insignificant influence of the degree of substitution of the hydroxy-groups of cellulose by acetate groups on the poly(ethylene glycol)–cellulose ether interaction. For cellulose acetate with $\gamma \geqslant 0.63$, the poly(ethylene glycol)–cellulose acetate interaction is hindered. One of the possible causes of this is, in our view, the enhancement of the solvation of the cellulose acetate macromolecules with increase in the number of unsubstituted OH groups in the polymer.

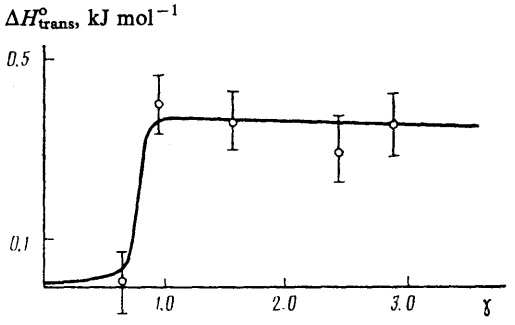



**Figure 16. Dependence of the enthalpy of transfer of poly(ethylene glycol) from DMSO to a solution of cellulose acetates at the initial concentration $c_{init}$ on the degree of substitution $\gamma$.**

Thus the experimental enthalpy of solution data presented make it possible to consider the thermochemical characteristics of non-aqueous solutions of cellulose and its derivatives from a single standpoint based on the allowance for the EDA capacity of the polymer and the solvent and also to discover the principal characteristics of the influence of the physicochemical properties of the solvents on the enthalpies of transfer of the probes in concentrated solutions of cellulose ethers.

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