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STATE AND SOLVATION OF WATER H/D ISOTOPOLOGUES IN APROTIC DIPOLAR ORGANIC MEDIA BASED ON RESULTS OF THERMOCHEMICAL INVESTIGATIONS

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Based on the analysis of thermochemical data on the study of solvation of H_2O and D_2O molecules and the state of them in aprotic dipolar organic media, being available in the literature including the results of own calorimetric measurements by the authors, three groups of solvents were identified in the given review. They differ in the nature of specific interaction with water H/D isotopologues. The first group consists of moderately electron-donating tetrahydrofuran (THF), para-dioxane (DO), and acetone (Ac), solvents whose hydrogen-bonds with the solute water are not much inferior in energy to those being formed between H_2O or D_2O molecules. The effects of heterocomponent H(D)-bond formation in the solvents of second group consisting of the predominantly electron-accepting propylene carbonate (PC), acetonitrile (AN), and nitromethane (NM) are largely caused by the availability of their donor-acceptor centers to interact with water isotopologue molecules. In this sense, PC corresponds in overall to the solvents from first group, while steric inconsistencies for the interaction of AN and, especially, NM with H_2O or D_2O molecules decrease appreciably the hydrogen-bonding contribution to forming the water-containing "solvation complex". The process of solvation of H_2O or D_2O molecules in solvents of the third group, namely, in N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), hexamethylphosphotriamide (HMPT), and dimethylsulphoxide (DMSO), where electron-donating abilities are higher than that of water, on the contrary, is accompanied by the formation of energetically more stable heterocomponent H- or D-bonds, compared to those existing in the "unary" aqueous medium. It was found that D_2O–H_2O isotope effects (IE) in the standard molar enthalpy of water solvation are in rather good correlation with the energy of hydrogen bonding between H_2O and an aprotic dipolar solvent. The specified enthalpy-isotope effects of solvation are also correlated in overall with the half-sum of donor and acceptor numbers (according to Gutmann) relating to the aprotic dipolar organic media being compared. The possibility of plotting the correct dependence of IE in the standard molar enthalpy of water solvation in amides on the solvent structuredness parameter (according to Ohtaki) was illustrated, too.

Keywords:

water H/D isotopologues, aprotic dipolar organic solvents, standard molar enthalpies of dissolution and solvation, isotope effects, hydrogen-bonding, donor-acceptor properties

Introduction

It is known that the uniqueness of liquid water as a "pure" (unary) solvent is determined by the ability of its molecules to form a three-dimensional (3D) continuous or continuum network of hydrogen bonds of different configurations. From the point of view of the manifestation of water space-coordinated structure features both in specific (through H-bonds formation) intermolecular interactions and in hydrophobic effects, a rather impressive database on the properties of diluted water solutions of organic non-electrolytes has been created up to the present moment. However, the information available in the literature on the study of water as a dissolved substance in organic media (including ionic liquids, which are of particular interest at present) of different nature is still extremely limited [1-35]. At the same time, considering non-aqueous (organic) solvent as one of the effective means of controlling a fine chemical process, one should keep in mind that the fact of the presence (and sometimes absence) of water micro-impurities in the reaction medium entails rather serious consequences, which end, among others, with the replacement of the solvent itself [7, 11]. Since water dissolved in microquantities in an organic solvent medium loses its characteristic (openwork) structure and with it many unique properties, its molecules (dimers, clusters) have a significant perturbing effect on the "solvate environment". This leads to a qualitatively new solvent with physicochemical and thermodynamic properties different from those of the anhydrous unary component [4, 6-8, 11].

On the other hand, the structural behavior of water in the case of extremely low water content in an organic solvent, where the three-dimensional hydrogen bonding network characteristic of the aqueous medium is absent, remains poorly understood. Therefore, the study of the state and solvation of water molecules in liquid media of organic origin, as well as the nature of their effect on the structure and thermodynamic characteristics of the surrounding solvent is an important task of both solution physicochemistry and modern technologies based on the use of non-aqueous systems. These include, first of all, technological processes of fine organic synthesis and separation/extraction of liquid systems, as well as processes aimed at obtaining high-purity compounds [4, 6, 8].

It is known that the "depolymerization" of water is directly related to the chemical nature of the solvent (or solvating) organic medium, i.e., its molecular structure and donor-acceptor capacity. From this point of view the *aprotonic dipolar* solvents, denoted further in the formulas by the subscript "1", are of significant interest. Formally, this class of solvents includes liquids that have a relative dielectric permittivity ε_1 and the dipole moment of the molecule μ_1 of at least 15 units and 2.5 Debye (D), or ~$8.3 \cdot 10^{-30}$ Kl·m, respectively [36-38]. Molecules of such liquid-phase compounds are not able to be hydrogen bond donors because their C-H bonds are not strongly polarized enough. However, due to the presence of undivided electron pairs at atoms of oxygen, nitrogen, phosphorus, sulfur, etc. in molecules of this kind, they can enter into sufficiently strong specific interactions (through the formation of strong H-bonds) with molecules of dissolved water, which have a pronounced electron acceptor capacity [38-40]. The structural and thermodynamic properties of aprotonic dipolar solvents are directly related to their properties in solutions extremely or highly diluted with respect to water [11]. Since the organic media in question are used in numerous processes and experimental devices, which involve the presence of water (often in the form of atmospheric moisture), the availability of reliable thermodynamic and physicochemical data for such water-containing solvents is an absolute prerequisite for the successful implementation of the practical and theoretical tasks set. Moreover, as was already emphasized above, the intensity and direction of structural changes and intermolecular interactions in each aprotonic dipolar medium under the influence of water microadditions depend largely on the donor-acceptor properties of the solvate environment.

The results of studies conducted in this field of solution physicochemistry show that, along with IR spectroscopic analysis [4-6, 8-10, 17], data on standard molar thermodynamic characteristics of water dissolution provide indispensable information on both the interactions of dissolved aqueous component with solvent and on the structural features of the resulting binary system. These characteristics are known to carry information only about the structural-average or *supramolecular* properties of the liquid-phase system [6, 7, 11]. Therefore, the necessary information on the structural and energetic aspects of intermolecular "heterocomponent" interactions at the microlevel can be obtained only indirectly, using various approaches and approximations [11, 15-18]. However, a number of problems are avoided when investigating the thermodynamic properties of H/D-isotope analogues of water (H_2O and D_2O: hereafter in the formulas - "2") in the same aprotonic dipolar organic solvent. The D_2O-H_2O-isotope effects (IE: δ) of dissolved matter, due to its quantum nature of origin [1, 41-44], provide sometimes indispensable information about the nature of intermolecular specific interactions and structural transformations in the newly formed "solvate complex" water - organic solvent.

The most informative in this sense were the data on IE in the volumetric and enthalpy characteristics of water solvation in the organic media under consideration. At the same time, while a considerable amount of space has been devoted to a comprehensive discussion of the volume-isotope effects of water dissolution and solvation in aprotonic dipolar solvents both in separate reviews [11, 45] and in periodic publications [12-15, 22, 24-28, 46-50], the information available in the literature on such enthalpy isotope effects is rather fragmented and has not been systematized earlier. As a consequence, some questions concerning the thermodynamic state of dissolved water still remain unanswered. One of them, perhaps the most important one, is related to the establishment of peculiarities of interaction of water molecules with the solvating medium depending on the structural (electronic) configuration of the latter. Generalizing our previous studies and the works of other authors, in this brief review we have tried to fill this "gap" based on the analysis of data on IE in the enthalpy of solvation of water and their relationship with the properties of the discussed class of solvents.

Comparative characterization of H/D-isotopes of water and aprotonic dipolar solvents of organic nature

The analysis of structural-energetic transformations occurring in the liquid medium of aprotonic dipolar organic solvent under the influence of H_2O molecules dissolved in it on D_2O is impossible without involving data on the physical and chemical properties of the components of the formed *standard* binary solution. According to IUPAC recommendations [51, 52], its state in a hypothetical ideal solution of unit concentration ($c_2^o = 1$), in which molecules are in the same energy state as in an infinitely diluted by component 2 solution, is taken as the standard state of the dissolved substance (2) in solution. The standard solvent state (1) in solution is the pure solvent state at pressure ~ 0.1 MPa and "current" temperature. In other words, the standard state postulates the hypothetical existence of molecules of the dissolved substance (in our case - water) exclusively in monomeric form surrounded by an infinitely large number of solvent molecules. Obviously, in such a solution the concentration-dependent 2-2-interactions should be completely absent. This assumption greatly facilitates the interpretation of thermodynamic effects induced by 1-2-interactions in a water-containing organic medium [11, 16, 45].

The very important question of the nomenclature of isotopic forms of deuterosubstituted compounds also cannot be ignored. Based on the IUPAC terminology [53], isomeric compounds that have the same number of isotopic atoms of each species in the gross formula of the molecule are called *isotopomers*. These include, for example, the methanols CH_3OD and CH_2DOH or CD_3OH and CHD_2OD. In turn, molecules that differ from each other only by their isotopic composition are commonly referred to as *isotopologues*. The latter include water isotopologues — H_2O and D_2O, which gives us a reason to use these names further in the discussion of enthalpic solvation effects in aprotonic dipolar organic media with isotope-different forms of the dissolved water component.

Since this review deals with the thermodynamic characteristics of H/D-isotopes of water as a dissolved substance, it is not necessary to focus on the analysis of structural and other differences of the compared aqueous media. Information on the properties of H_2O and D_2O molecules can be found, for example, in [11, 42, 54]. The H/D isotopes of water have been shown to consist of sp^3-hybridizing atomic orbitals of molecules with large but insignificantly different μ_2 dipole moments (Table 1). One of the main reasons for the change in μ_2 is the quantum effect, which is determined by the difference in amplitudes of the anharmonic zero oscillations of molecules H_2O and D_2O. The latter circumstance also causes a change in the inter-nuclear distances in the water molecule and, as a consequence, its van der Waals volume $v_{vdw,2}$. Thus, O–H → O–D substitution induces a ~3% bond reduction [44], while the values of v_{vdw}, 2 are 0.07 nm^3 [11, 55]. In turn, this leads to a change in the donor-acceptor properties of the water molecule, i.e., its ability to form hydrogen bonds with neighboring molecules. According to the findings [11, 56], the consequence of electron density redistribution in molecular quantum-chemical complexes of water when H_2O is replaced by D_2O is the enhancement of electron acceptor and attenuation of electron donor ability (AN_2 and DN_2 values in Table 1, respectively) in deuterated isotope. This factor, along with a decrease in the frequencies of librations (torsional vibrations) and valence strain vibrations of the intramolecular O-H bond during the proton replacement by a deuteron, predetermines an increase in the dissociation energy of hydrogen bonds in heavy water [11, 41-43]. According to the results of [42, 57], the IE in hydrogen bonding energy of water-water $\delta E_{vc,2\text{-}2}(H_2O \rightarrow D_2O)$ is -(1.2 ± 0.2) kJ·mol^{-1} in the "background" of well correlated H-bond energy value in a medium of ordinary (protonated) water: $E_{wb,2\text{-}2} = -(15.5 \div 16.0)$ kJ-mol^{-1} [8, 11, 15, 58].

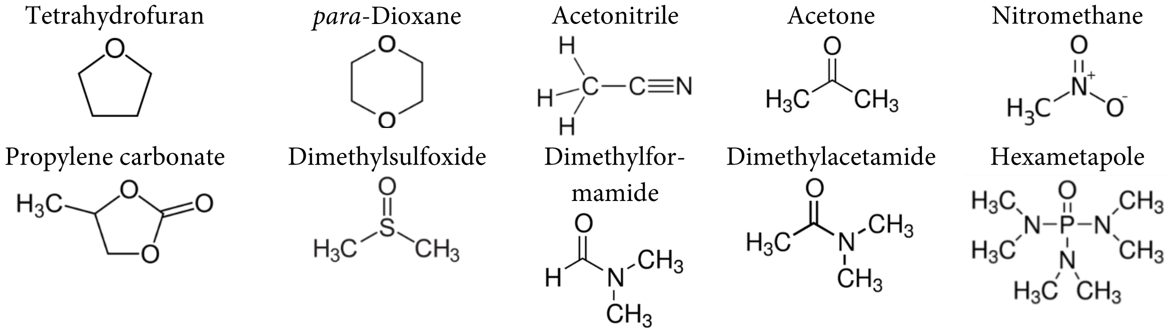

Fig. 1. Structural formulas of aprotonic dipolar solvent molecules

The review of literature sources on the problem under discussion revealed the information on the standard enthalpic dissolution characteristics of H_2O and D_2O ($\Delta_p H_2^o$) in ten aprotonic dipolar solvents of organic nature (Fig. 1): acetone (Ats) [59, 60]; acetonitrile (NA) [46, 61]; *N,N*-dimethylacetamide (DMAA) [62]; *N,N*-dimethylformamide (DMF) [62]; dimethyl sulfoxide (DMSO) [62]; *para*-(1,4-)-dioxane (DO) [60,63]; hexamethylphosphotriamide, or hexametapol (HMFTA) [62, 64]; nitromethane (NM) [61,64]; propylene carbonate (PC) [61] and tetrahydrofuran (THF) [60, 65]. At the same time, the values of $\Delta_p H_2^o$ given in the above papers mostly refer exclusively to $T = 298.15$ K as the most frequently used ("reference") temperature in thermochemical studies of liquid-phase systems. Comparative characteristics of the listed solvents are given in Table 1.

Table 1. Physico-chemical properties of aprotonic dipolar solvents and H/D-isotopes of water that determine their ability to intermolecular interaction at $T = 298.15$ K and $p = 0.1$ MPa

Medium	*DN*	*AN*	S_p	ε	μ
THF	20.0	8.0	7.16	7.58	1.75
DO	14.8	10.8	10.0	2.21	0.45
Ac	17.0	12.5	5.48	20.6	2.69
NM	2.7	20.5	24.0	38.0	3.56
AN	14.1	18.9	12.5	36.0	3.44
PC	15.1	18.3	12.4	65.0	4.98
DMSO	28.9	19.3	13.7	46.7	3.96
DMFA	26.6	16.0	12.5	36.7	3.86
DMAA	27.8	13.6	16.6	37.8	3.72
HMFTA	38.8	10.6	0.39	29.6	5.54
H_2O	18.0	54.8	19.3	78.4	1.84
D_2O	< (↑)	> (↑)	20.7	78.2	1.86

According to the generally accepted classification based on *Lewis*'s theory of acids and bases and *Brønsted-Lowry*'s protolytic theory, the organic solvents in Table 1 are conventionally divided into three categories [36, 40]. These are: *aprotonic protophobic* (Ac, NA, NM and PC), *aprotonic protophilic* (HMFTA, DMAA, DMFA and DMSO) and *electron donors with low dielectric constant* (DO and THF). It should be noted that the last two solvents under the formally established conditions (see above) should not be referred to the class of aprotonic dipolar liquids because of too low values of dielectric permittivity of the medium (ε_1) and dipole moment of the molecule (μ_1). However, based on the objectives of this review study, other, more informative physico-chemical properties that predetermine the ability of each of the solvents listed in Table 1 to interact with dissolved water isotope molecules should be relied upon. According to the conclusions [36-40], among semiempirical parameters reflecting at the molecular level the balance of acid-base properties of the solvent in chemical processes, the main ones are electronic donor and acceptor numbers. In Table 1, they are represented by *AN* and *DN* values on the *Gutmann* scale [38-40]. According to the definition [39], *AN* is a dimensionless quantity, and *DN* values measured in kcal-mol^{-1} are not commonly expressed in the SI unit system, and, as a rule, they are postulated to be conditionally dimensionless. This is also the dimensionless *Otaki* parameter [40, 66] (S_p values divided by kJ·mol^{-1}, in Table. 1), which is identical to the energy of intermolecular interaction in a hypothetical "three-dimensional molecular ordering" in a liquid: $S_p = \Delta_{evp}H - DA - VDW$, where $\Delta_{evp}H$ is enthalpy of liquid evaporation and DA and VDW are energies of donor-acceptor and other (van der Waals) interactions respectively. The value of DA is calculated as $4.184 \cdot 10^{-2} \cdot f_{DA} \cdot DN \cdot AN$, where $f_{DA} = 1$ (for water: $f_{DA} = 0.5$, for AN: $f_{DA} = 0.8$), and $VDW = 0.222V$ (where V is the molar volume of solvent). Note also that μ in Table 1 is expressed in Debyes (1 D = $3.33564 \cdot 10^{-30}$ Cl·m).

The analysis of the data in Table 1 in terms of the variation of solvent "interaction parameters" allows us to distinguish three general groups of aprotonic dipolar media in which characteristic trends of DN_1 and AN_1 are observed. The first of these contains Ac, DO, and THF, which are moderately electron-donating solvents whose AN_1 values are lower than those of the water isotopologues and other solvents in Table 1 (excluding HMFTA). The second group consists of AN, NM and PC, which are predominantly electron-accepting solvents, while DMAA, DMFA, DMSO, and HMFTA form the third group - predominantly electron-donating solvents (their *DN* values are higher than those of water and other liquid isotopes in Table 1). Although such a division is rather tentative, it allows us to reveal some regularities in the variation of both $\Delta_p H_2^o(H_2O)$ and $\Delta_p H_2^o(D_2O)$ and the corresponding IEs depending on the donor-acceptor nature of the solvating medium.

Enthalpy characteristics of dissolution and solvation of H_2O and D_2O

As mentioned above, H_2O/D_2O-isotope substitution, which is inherently a quantum effect, is a very "subtle" tool for analyzing changes in structure and intermolecular interactions, including "H-bonding" effects induced by the presence of dissolved water molecules. Therefore, when replacing H_2O with D_2O in organic media, it seems important to perform calorimetric measurements [67] under the same conditions and with the same set of solvents.

Table 2 compiles available data in the literature on $\Delta_p H_2^o$ for H_2O and D_2O as dissolved substances in aprotonic dipolar solvents. Basically, the given standard molar enthalpy characteristics were determined by averaging the results of calorimetric measurements of the integral thermal effects of dissolution of water isotopes in the studied media at $T = 298.15$ K. For comparison, Table 2 also contains selected common values of $\Delta_p H_2^o$ for ordinary water. In addition, the data in italic on $\Delta_p H_2^o$ (see Table 2) were obtained by extrapolating (to infinite dilution) the dependences of the reduced molar enthalpy of mixing H^E/x_2 on the molar fractional content of the water isotope x_2 in the solutions diluted relative to it [46, 59, 65]. Since the statistical sample of available experimental data by $H^E(x_2)$ was clearly insufficient for an adequate mathematical description of the organic solvent-rich mixture composition region ($x_2 < 0.05$ m.p.a.), the validity of the data obtained in this manner (i.e., through excess enthalpies) of $\Delta_p H_2^o$ values in general leaves much to be desired (see Table 2). For a number of systems, however, the scatter of $\Delta_p H_2^o$ values obtained and "direct calorimetric" dissolution effects of water isotopologues is very noticeable. First of all, this applies to the discussed data for water-containing media DO, NM, PC and DMAA. At the same time, it is not the difference in absolute values of $\Delta_p H_2^o$ that is decisive here, but the way in which the corresponding IEs are related: $\delta\Delta_p H_2^o(H_2O \rightarrow D_2O)$.

Taking this into account, only the results of calorimetric measurements obtained earlier by the staff of ICR RAS (Ivanovo), namely by one of the authors of this review together with *Smirnov* [60-62], as well as data of *Batov* for the systems {DMAA + H_2O (D_2O)} and {HMPT + H_2O (D_2O)} [64] (results marked in bold in Table 2) will be discussed further. The reason for this choice, as we have already noted above, is the "strict" observance of the same experimental conditions in conducting research and system analysis in the mentioned works.

Table 2. Standard molar enthalpies of H_2O and D_2O dissolution, $\Delta_p H_2^o$ (kJ·mol^{-1}), in comparable aprotonic dipolar solvents at $T = 298.15$ K and $p = 0.1$ MPa

Medium	**$\Delta_p H_2^o(H_2O)$**	**$\Delta_p H_2^o(D_2O)$**
THF	4.28 ± 0.04 [60]	4.84 ± 0.02
	4.59 ± 0.09 [65]	*5.03 ± 0.09*
	4.36 ± 0.03 [68]	–
DO	6.09 ± 0.04 [60]	6.47 ± 0.02
	6.29 ± 0.02 [63]	6.62 ± 0.02
	6.08 ± 0.17 [68]	–
Ac	4.33 ± 0.05 [60]	4.76 ± 0.04
	3.68 ± 0.11 [59]	*3.91 ± 0.10*
	4.39 ± 0.05 [69]	–
NM	12.82 ± 0.02 [61]	13.85 ± 0.03
	12.63 ± 0.03 [64]	13.47 ± 0.04
AN	7.92 ± 0.05 [61]	8.63 ± 0.06
	7.80 ± 0.02 [46]	*8.58 ± 0.03*
	7.91 ± 0.05 [69]	–
PC	8.25 ± 0.06 [61]	8.60 ± 0.05
	8.19 ± 0.05 [69]	–
	8.08 ± 0.08 [70]	–
DMSO	-5.38 ± 0.05 [62]	-5.24 ± 0.04
	-5.44 ± 0.05 [8]	–
	-5.40 ± 0.04 [70]	–
DMFA	-3.55 ± 0.04 [62]	-3.47 ± 0.04
	-3.60 ± 0.04 [69]	–
DMAA	-5.61 ± 0.03 [62]	-5.45 ± 0.03
	-5.92 ± 0.03 [64]	-5.75 ± 0.07
	-5.65 ± 0.05 [69]	–
HMFTA	-7.40 ± 0.05 [64]	-7.50 ± 0.02

According to Table 2, the dissolution process of H_2O and D_2O in the solvents of the first and second groups we identified is accompanied by heat absorption. The endothermicity of the effect in question becomes generally more pronounced at the transition from (THF, Ac, and DO) to (AN, PC and NM). In the third group of aprotonic dipolar solvents (see Table 2), on the contrary, water isotopes dissolve with an exothermic effect, which becomes more and more noticeable at the transition from DMFA to DMSO and DMAA and further to HMFTA. It should also be noted that $\Delta_p H_2^o$ is comparable (within the experimental error) in those cases where THF and Ac or AN and PC pairs as solvate media are considered separately. The same is true for the DMSO/DMAA solvent pair, where the difference in $\Delta_p H_2^o$ is only 0.2 ÷ 0.3 kJ·mol^{-1} (see Table 2). On the other hand, the endothermicity of the dissolution process of the water isotope increases almost twofold in the transition from the first solvent group to the second, and within each of these groups there is an increase in $\Delta_d H_2^o$ (almost 150%) in the case of transition to DO or NM (see Table 2). In the third group of solvents, the fact that the dissolution effects of H_2O and D_2O in *N,N*-dimethylsubstituted amides differ by ~2 kJ·mol^{-1}, despite the obvious similarity of the interaction characteristics of DMFA and DMAA given in Table 1, is unusual. At the same time, the exothermicity of the dissolution process of the water isotope in HMFTA is more than twice as high as $\Delta_p H_2^o$ in DMF, and exceeds the corresponding effect for H_2O and D_2O in DMSO or DMAA by the same ~2 kJ·mol^{-1} (in absolute value).

In order to understand the reasons for the change of $\Delta_d H_2^o$ in the transition from one solvent group to another (and within each group), it is necessary to keep in mind that this characteristic actually reflects the difference in the energy of interaction of H_2O or D_2O molecules with the solvate environment and with their own similar ones in the aqueous medium itself (*in bulk*) [11, 16, 68]. Indeed, the enthalpic dissolution effect of the water isotope ($\Delta_d H_2^o$) can be represented as two components:

$$\Delta_d H_2^o = \Delta_s H_2^o + \Delta_{evp} H_2^* = \Delta_s H_2^o - \Delta_{cond} H_2^*, \quad (1)$$

where $\Delta_s H_2^o$ is the standard molar enthalpy of H_2O or D_2O, and $\Delta_{evp} H_2^*$ and $\Delta_{cond} H_2^* (\equiv -\Delta_{evp} H_2^*)$ are the molar enthalpy characteristics of water isotope evaporation and condensation processes respectively. That is, the solvation of water can be identified with the condensation of one mole of its gaseous molecules in an infinitely large amount of an aprotonic dipolar solvent. Hence, the positive/negative sign at the value $\Delta_d H_2^o$ suggests that the 2–1-interaction should be weaker/stronger than the interaction between H_2O or D_2O molecules in isotopically divergent aqueous media. The main contribution to $\Delta_p H_2^o$ is due to two effects related to (i) the energy input to the solvate cavity in the solvent (positive contribution) and (ii) the heat release during the formation of the "solvate complex", or the molecular association of ordinary or heavy water with the surrounding solvent due to H- or D-bonds (negative contribution) [60-62, 65]. Hence, the sign and the numerical value of $\Delta_d H_2^o$ in Table 2 are determined by which of these two enthalpic effects is dominant.

At the same time, it should be kept in mind that the values of $\Delta_d H_2^o$ and the corresponding IE, $\delta\Delta_d H_2^o(H_2O \rightarrow D_2O)$, cannot provide full information on the energy changes in the solvent structure induced by the solvation process of water molecules due to the existing difference in the value of $\Delta_{evp} H_2^*$ for water isotopes in equation (1). Since the replacement of H_2O with D_2O $\Delta_{evp} H_2^*$ increases from 44.00 to 45.39 kJ·mol^{-1} at $T = 298.15$ K [11, 42], this difference is almost 1.4 kJ·mol^{-1}(!). In other words, to compare the solvation effects of H_2O on D_2O in the same aprotonic dipolar solvent, the amount of energy expended to break the structural packing of each of the water isotopologues should be considered:

$$\delta\Delta_s H_2^o(H_2O \rightarrow D_2O) = \delta\Delta_d H_2^o(H_2O \rightarrow D_2O) - \delta\Delta_{evp} H_2^*(H_2O \rightarrow D_2O). \quad (2)$$

Table 3. Standard molar enthalpies of H_2O and D_2O solvation, $\Delta_s H_2^o/(\text{kJ·mol}^{-1})$, in comparable aprotonic dipolar solvents at $T = 298.15$ K and $p = 0.1$ MPa

Medium	$-\Delta_s H_2^o(H_2O)$	$-\Delta_s H_2^o(D_2O)$
THF	39.72 ± 0.04 [60]	40.55 ± 0.02
DO	37.91 ± 0.04 [60]	38.92 ± 0.02
Ac	39.67 ± 0.05 [60]	40.63 ± 0.04
NM	31.18 ± 0.02 [61]	31.54 ± 0.03
AN	36.08 ± 0.05 [61]	36.76 ± 0.06
PC	35.75 ± 0.06 [61]	36.79 ± 0.05
DMSO	49.38 ± 0.05 [62]	50.63 ± 0.04
DMFA	47.55 ± 0.04 [62]	48.86 ± 0.04
DMAA	49.61 ± 0.03 [62] 49.92 ± 0.03 [64]	50.84 ± 0.03 51.14 ± 0.07
HMFTA	51.40 ± 0.05 [64]	52.89 ± 0.02

Table 3 shows the values of the standard molar enthalpy of solvation of water isotopes $\Delta_s H_2^o$ in the aprotonic dipolar solvents, calculated from equation (1), assigned to various groups of organic media according to the nature of their interaction with dissolved H_2O and D_2O molecules. Analysis of the data in Table 3 allows us to conclude that in all systems under consideration, in general, there is an intensification of water solvation as a result of deuteration of its molecules (i.e., $\delta\Delta_s H_2^o < 0$). To detail the trends of IE in the standard dissolution and solvation enthalpies of water, $\delta\Delta_d H_2^o(H_2O \rightarrow D_2O)$ and $\delta\Delta_s H_2^o(H_2O \rightarrow D_2O)$, a comparison of numerical data on these thermodynamic characteristics in correlation with their properties as solvent (see Table 1) as well as the solution. Such data are contained in Table 4, along with information available in the literature on the H-bonding energy of water - organic solvent, $E_{wb,2\text{-}1}$, referred to the mole of hydrogen bonds.

Table 4. D_2O-H_2O-isotopic effects in the standard molar enthalpies of dissolution, $\delta\Delta_d H_2^o/(kJ\cdot mol^{-1})$, and solvation, $\delta\Delta_s H_2^o/(kJ\cdot mol^{-1})$, of water in the compared aprotonic dipolar solvents, and the H-bond energy values between solution components, $E_{wb,2\text{-}1}/(kJ\cdot mol^{-1})$, at $T = 298.15$ K

Medium	$\delta\Delta_d H_2^o(H_2O \rightarrow D_2O)$	$\delta\Delta_s H_2^o$	$E_{wb,2\text{-}1}$
THF	0.56 ± 0.04 [60]	-0.83	-13.0
DO	0.38 ± 0.05 [60]	-1.01	-13.8
Ac	0.43 ± 0.06 [60]	-0.96	-13.5
NM	1.03 ± 0.04 [61]	-0.36	-8.8
AN	0.71 ± 0.08 [61]	-0.67	-12.3
PC	0.35 ± 0.08 [61]	-1.04	-14.0
DMSO	0.14 ± 0.06 [62]	-1.25	-17.2
DMFA	0.08 ± 0.06 [62]	-1.31	-16.8
DMAA	0.16 ± 0.04 [62] 0.17 ± 0.08 [64]	-1.23 -1.22	-17.8
HMFTA	-0.10 ±0.06 [64]	-1.49	-18.8

Note that the values of $E_{wb,2\text{-}1}$ collected in Table 4 are borrowed from several literature sources, the authors of which, in turn, used various experimental (thermodynamic, spectroscopic, etc.) approaches to determine the characteristic in question. As a consequence, for a number of the aprotonic dipolar media presented in Table 4, there is a significant scatter in the $E_{wb,2\text{-}1}$ data. Suffice it to say that the $E_{wb,2\text{-}1}$ values estimated in [4, 58] for the system (Ac + H_2O) show almost two-fold difference, changing from -11.3 to -20.2 $kJ\cdot mol^{-1}$. The situation is not much better for water solutions in DO and AN: in the first case, the considered parameter "fits" in the range (-10.5 ÷ -13.8) $kJ\cdot mol^{-1}$ [1, 4, 8, 69, 70], while in the second case it changes from -9.6 to -15.0 $kJ\cdot mol^{-1}$ [1, 4, 70]. Taking into account the rather large error in the determination of $E_{wb,2\text{-}1}$ (1 ÷ 2 $kJ\cdot mol^{-1}$), $E_{wb,2\text{-}1}$ values based on NMR and IR spectroscopic measurements [1, 4, 70] for Ac, DO, NM and DMSO were chosen as the "reference" values (see Fig. tab. 4). A similar value for a standard solution of water in AN was obtained by averaging the data [1, 4, 15, 69]. Single data on the values of $E_{wb,2\text{-}1}$ for the systems (THF + H_2O) and (PC + H_2O) are contained in [25, 65]. As for the corresponding data for water in amides (DMFA, DMAA and HMFTA), these are the most correlated in the available sample of literature [8, 69-71].

In the literature there are practically no data on IE in the hydrogen bonding energy of water - aprotonic dipolar solvent ($\delta E_{wb,2\text{-}1}$). Therefore, it seems logical to use further the values of $\delta\Delta_s H_2^o(H_2O \rightarrow D_2O)$ as such a measure (see Table 4).

D_2O-H_2O enthalpy-isotope effects of solvation in aprotonic dipolar solvents of organic nature

As follows from the data in Table 4, the positive enthalpy-isotope effect of water dissolution process (taking into account the error of its determination) increases in the sequence: DMFA ≤ DMSO ≈ DMAA < PC ≈ DO ≤ Ac < THF < AN < NM. Two things stand out here. First, based on the trends in $\Delta_d H_2^o$ in Table 2, two cyclic esters, DO and PC, "drop out" from the series in question. Low positive IE values in $\Delta_d H_2^o$ in the above solvents, given the peculiarities of their structure and properties (see Fig. 1 and Table 1), can be explained by the greater availability of electron-donor centers in the molecular cycle for the formation of hydrogen bonds with water isotope molecules. On the contrary, steric effects contribute to the attenuation of H_2O and especially D_2O solvation in the predominantly electron acceptor NM due to the formed conformation with an antiparallel arrangement of H-O-H and O-N-O bonds similar in geometry [5, 61]. In general, this predetermines the "purely dipolar" nature of the interaction between the solution components. Secondly, quite unusual in Table 4 is the fact that the exothermicity of dissolution of water at deuterating its molecules in DMSO, DMFA, and DMAA environments seems to decrease, which contradicts the "classical" ideas about the differentiating influence of H/D-isotope substitution on enthalpy effects in solutions [46, 48, 56, 59-65]. In particular, if a donor-acceptor compound such as water dissolves with an exo-effect, the IE value $\delta\Delta_d H_2^o(H_2O \rightarrow D_2O)$ should be negative, as in the case of the formation of a water solvato-complex in HMFTA (see Table 4). Obviously, the observed inversion of the sign $\delta\Delta_d H_2^o$ in the series of aprotonic protophilic solvents from the third group in Table 4 is also related to the different ability of H_2O and D_2O molecules to incorporate into the initial structural matrix of the solvating medium. However, these differences are rather insignificant, given that the IE under consideration is either generally comparable with the error of its determination (in DMFA) or exceeds the latter in absolute value only by no more than two times (in DMSO and HMFTA).

The trends of $\delta\Delta_d H_2^o$ in Table 4 are directly related to the nature of the evolution of enthalpine-isotope effects of water solvation, which, as mentioned above, carry more complete information on the energy changes in the structure of the aprotonic dipolar solvent under the influence of H_2O and D_2O molecules. First of all, it should be noted that the absolute values of $\delta\Delta_s H_2^o(H_2O \rightarrow D_2O)$ increase in the direction directly opposite to the above series of IE in $\Delta_p H_2^o$, with a maximum for the system (HMFTA + water). Attempts to correlate $\delta\Delta_s H_2^o$ with the donor, acceptor, or other properties of solvents of all three groups under consideration in general (see Table 1) did not yield a satisfactory result. At the same time, analyzing the data in Table 4, one can conclude that there is a functional correspondence between the IE in $\Delta_s H_2^o$ and the value of $E_{wd,2\text{-}1}$, characterizing the strength of heterocomponent hydrogen (H- or D-) bonds in the solvato-complex of water. The possibility of constructing such a correlation, despite the subjectivity of estimating some of the $E_{wd,2\text{-}1}$ values in Table 4, is illustrated in Fig. 2.

In the analytical form, the one shown in Fig. 2 the correlation dependence can be expressed in the form of the first order equation (indicated by the dashed line):

$$E_{wd,2\text{-}1}/(\text{kDj}\cdot\text{mol}^{-1}) = -5.6(\pm 0.8) + \\ + 8.9(\pm 0.7)\cdot \delta\Delta_s H_2^{o}; \quad r^2 \approx 0.94. \quad (3)$$

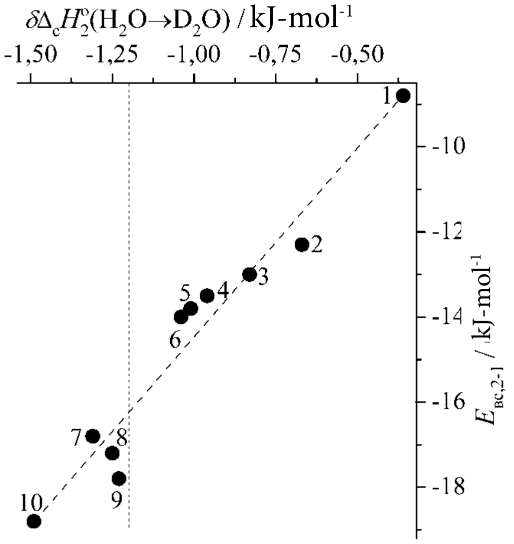

Fig. 2. Correlation relationship between hydrogen bonding energy of water - aprotonic dipolar solvent and H/D-isotope effect in the standard molar enthalpy of solvation of aqueous component: 1 – NM, 2 – NA, 3 – THF, 4 – Ac, 5 – DO, 6 – PC, 7 – DMF, 8 – DMSO, 9 – DMAA, 10 – HMFTA (T = 298.15 K)

It follows from (3) that in the aprotonic dipolar solvent medium with zero enthalpy isotope ($H_2O \rightarrow D_2O$)-effect of water solvation, the $E_{wd,2\text{-}1}$ value would be less than 6 kJ-mol^{-1} in absolute terms. In turn, in the case of the hypothetical state of a standard water solution without specific interactions, i.e., when Insert a tag $E_{wd,2\text{-}1} = 0$ in equation (3), the IE in $\Delta_s H_2^{o}$ would be positive (≈ 0.6 kJ-mol^{-1}). Another important feature of the one shown in Fig. 2 correlation is the presence of two distinct regions separating the solvents under study by their ability to interact with water molecules {dotted lines correspond to the values of $E_{wd,2\text{-}2}$ and $\delta E_{wd,2\text{-}2}(H_2O \rightarrow D_2O)$}. When $E_{wd,2\text{-}1} > E_{wd,2\text{-}2}$, the value of $\delta\Delta_s H_2^{o}$ exceeds in absolute value the IE in hydrogen bonding energy of water-water. These include DMSO, DMFA, DMAA and HMFTA, which are predominantly electron-donating solvents with $DN_1 >> DN_2$ (see Table 1). Conversely, a "family" of solvating media with $E_{wd,2\text{-}1} < E_{wd,2\text{-}2}$ and $|\delta E_{wd,2\text{-}2}| > |\delta\Delta_s H_2^{o}|$ form the solvents of the first two groups in Tables 1-4 (cf. Fig. 2). In other words, the general regularities in the change in the energy characteristics of the interaction of water isotope molecules with the solvate environment that we found confirm the assumptions available in the literature that HM, AH, THF, Ac, DO, and PC form less strong bonds with H_2O and D_2O than those existing in the aqueous environment.

As noted above, we were not able to establish a correlation (physically based) between the enthalpy-isotope effects of water solvation and the individual donor (DN_1) and acceptor (AN_1) characteristics of the aprotonic dipolar solvents from the sample presented in Tables 1 and 4. At the same time it is known that the change of many properties of solutions of non-electrolytes (and ionic compounds) when varying the structural nature of the solvent correlates well with the half-sum of the donor and acceptor numbers of the solvating medium: $0.5(DN_1 + AN_1)$ [72, 73]. Considering the fact that the donor and acceptor properties of water as a dissolved substance change during deuterosubstitution in its molecules [11, 56], we plotted the correlation dependence $\delta\Delta_s H_2^{o}(H_2O \rightarrow D_2O)$ on $0.5(DN_1 + AN_1)$ (see Tables 1 and 4), which is shown in Fig. 3.

As can be observed in Fig. 3, the behavior of most of the non-electrolyte systems discussed here is quite consistent with the predicted relationship between $\delta\Delta_s H_2^o(H_2O \rightarrow D_2O)$ values from $0.5(DN_1 + AN_1)$. The only exceptions are perhaps the effects of the interaction of water isotopologues with the solvate environment in NM, NA, DO, and DMSO. However, in our opinion, the indicated deviations from the correlation in question (see Fig. 3) have their own structure-based interpretation.

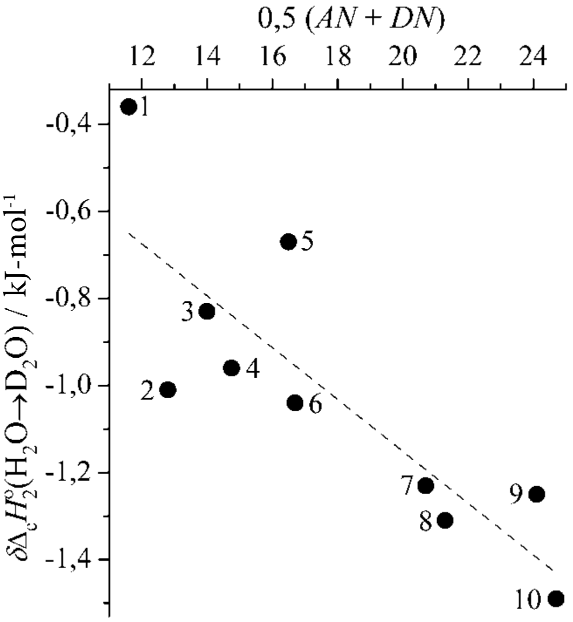

Fig. 3. Correlation between the H/D-isotope effect in the standard molar enthalpy of water solvation and the half-sum of the donor and acceptor numbers of the aprotonic dipolar solvent: 1 – NM, 2 – DO, 3 – THF, 4 – Ac, 5 – AN, 6 – PC, 7 – DMAA, 8 – DMFA, 9 – DMSO, 10 – HMFTA (T = 298.15 K)

Thus, the introduction of a second oxygen atom into the five-membered cycle of a *monoester* molecule (THF) to form a symmetrical molecule of a six-membered cyclic *diester* (1,4-DO) causes a noticeable reduction in the endothermicity of water dissolution during deuteration of its molecules (see Tables 2 и 4). The situation that has arisen is related to the mutual influence of two *para*-coordinated oxygen atoms, which causes the weakening of configuration effects in the transition to a standard solution of D_2O in DO [5]. This is crucial for moderately donor solvents of the first group (THF, DO, Ac) in the case of their interaction with the more electron acceptor D-isotope of water [1, 11, 14, 15, 22, 28, 60]. It is also worth noting the rather large values of $\delta\Delta_s H_2^o(H_2O \rightarrow D_2O)$, which are generally close to the IE in $E_{wd,2\text{-}2}$ (see Table 4), in the aprotonic dipolar media of this group, indicating their ability to form very strong hydrogen bonds with dissolved molecules of H_2O and D_2O.

The same can be said for standard solutions of H/D-isotopologues of water in predominantly electron-accepting PC (see Tables 1 and 4). In this case, the value $\delta\Delta_s H_2^o = -1.04$ kJ·mol^{-1} is in good agreement with the findings from NMR and IR spectroscopic measurements [74] that the molar enthalpy of water dimerization is only ~15% higher than the molar enthalpy of association of water and PC molecules. In turn, the other two solvents from the second group (HM and AN in Table 4), which "fell out" of the one presented in Fig. 3 correlations, *isodielectric* in structure (by virtue of identity of their values μ_1 and ε_1 in the Table. 1). However, in contrast to the $\Delta_{d(s)}H_2^o$data in NM, the enthalpy effects of dissolution and solvation of H_2O and D_2O in AN are even comparable to those in PC (see Tables 2 and 3), since the DN_1 and AN_1 values of these solvents differ only slightly (see Table 1). As we mentioned above, the main reason for such significant differences in $\delta\Delta_s H_2^o(H_2O \rightarrow D_2O)$ here is also the configuration factor that determines the measure of availability of donor-acceptor centers of HM, AN and PC molecules for their interaction with H_2O or D_2O molecules. In the most pronounced form, the steric effects should manifest themselves in the dissolution of H/D-isotopes of water in NM [75]. According to *Bonner and Choi* [5], because of the similarity of the geometry of the bonds H-O-H and

O-N-O, the water molecule occupies a position in which the three oppositely charged atoms of each of the H_2O and CH_3NO_2 molecules are adjacent to each other in the form of two overlapping "V". Hence, the formation of a heterocomponent H- or D-bond is problematic and the interaction between NM and water isotopologues is almost dipolar in nature.

The situation is somewhat different when comparing the $\delta\Delta_s H_2^o(H_2O \rightarrow D_2O)$ values in DMSO and *N,N*-dimethylsubstituted amides (the third group of solvents in Table 1). On the one hand, the unexpectedly large difference in $\Delta_s H_2^o$ for DMFA and DMAA (see Table 3) may be due to the fact that the methyl group attached to >C=O is more polarized and stabilizes the resonant form $^-O\text{-}\dot{C}\text{=}N^+$ to a greater extent than the formyl hydrogen atom in the DMFA molecule [27, 62, 76]. At the same time, being a stronger proton donor (see Table 1), the DMFA medium promotes the formation of C–H···O bonds (via the methyl group) with H/D isotopes of water, thus giving an additional negative contribution to $\delta\Delta_s H_2^o$, compared to that in the case of H_2O or D_2O solvation in DMAA (see Table 4). Since the donor-acceptor numbers of an aprotonic dipolar solvent are the main components of its structurization parameter S_p (see Table 1), it can hardly be considered surprising that this parameter, like the value of $0.5(DN_1 + AN_1)$ in Fig. 3, is in good correlation with $\delta\Delta_s H_2^o(H_2O \rightarrow D_2O)$ in the amides of the series under consideration (Fig. 4). Note that a similar relationship is not found when analyzing $\delta\Delta_s H_2^o$ and S_p values for solvents from other groups where $DN_1 < DN_2$ (except for THF).

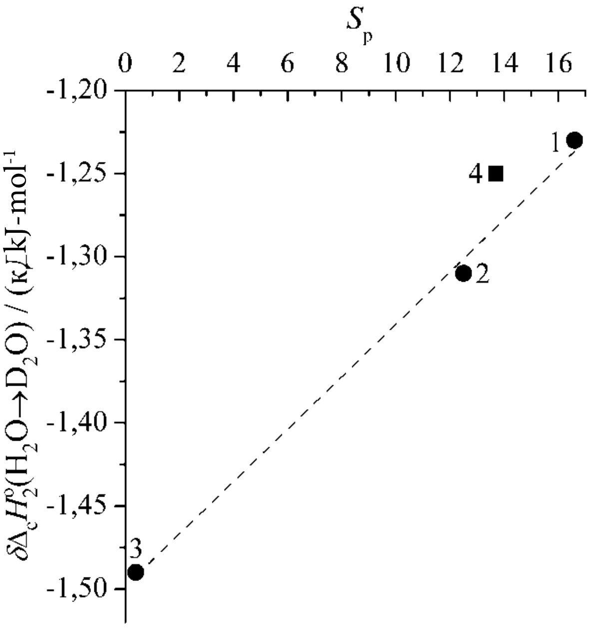

Fig. 4. Correlation between the isotopic effect in the standard molar enthalpy of water solvation and the "structurization parameter" [40, 66] of the aprotonic dipolar solvent: 1 – DMAA, 2 – DMFA, 3 – HMFTA, 4 – DMSO

Observed in Fig. 3 and 4 deviations of the data for DMSO from the "amide line" are primarily due to the presence of the sulfoxide group (>S=O) in the molecules of this solvent. The influence of the latter on the electronic configuration of the DMSO molecule causes an increase in both the basicity and the acidity of the solvating medium, compared to the values (DN_1) and (AN_1) for DMAA and DMFA (see Table 1). Moreover, DMSO and HMFTA have essentially comparable values of $0.5(DN_1 + AN_1)$ (see Fig. 3), indicating a high variability of the >S=O-group in specific contacts with dissolved water isotope molecules [77]. Moreover, according to [26], the structure of H_2O or D_2O solvatocomplex in DMSO is more densely packed than in the solutions of the compared amides. Hence, it can be assumed that the discussed non-ordinary behavior of H/D-isotopes of water in DMSO medium is largely due to the relative reduction of energy expenditure for the creation of the solvate cavity in this solvent.

Conclusions

Summarizing the above considerations, it should be noted that a systematic study of the enthalpy characteristics of water solutions in aprotonic dipolar or other proton acceptor media is a necessary step in understanding not only the structural-energetic effects in the solvent, but also the thermodynamic state of the dissolved component, devoid of the unique three-dimensional H-bond network present in liquid water. The results of the discussion of the problem raised in the review led us to the conclusion that the combined use of (micro)dissolution calorimetry and H_2O/D_2O-isotope substitution methods in water molecules appears to be one of the most informative thermodynamic approaches based on minimal "perturbation" of the solvent (solution) structure.

Perhaps the most important result of our study is the conclusion about the determining role of donor-acceptor interactions, including the effects of heterocomponent hydrogen bonding, in the process of water solvation in the compared aprotonic dipolar media. On this basis, three groups of solvents that differ in the nature of specific interaction with H/D-isotopes of water were identified. The first group is moderately electron-donor *para*-dioxane, tetrahydrofuran and acetone, which form hydrogen bonds with dissolved water and the energy of which is slightly less (by 2 ÷ 3 $kJ \cdot mol^{-1}$) than that between H_2O or D_2O molecules. The effects of the formation of heterocomponent H(D)-bonds in mainly electron acceptor solvents of the second group - nitromethane (NM), acetonitrile (AN) and propylene carbonate (PC) - are largely determined by the measure of availability of their donor-acceptor centers for interaction with molecules of H- or D-isotope water. While PC in this sense is more consistent with solvents of the first group, steric inconsistencies in the interaction of AN and, especially, HM with H_2O or D_2O molecules markedly reduce the share of hydrogen bonds in the total enthalpy effect of water solvatocomplex formation. The process of solvation of H_2O or D_2O molecules in the solvents of the third group - *N,N*-dimethylformamide, *N,N*-dimethylacetamide, hexamethylphosphotriamide and dimethylsulfoxide (DMSO), with a higher electron-donating capacity than that of water isotope, is accompanied by the formation of more energy stable heterocomponent H- or D-bonds as compared to those existing in "unary" aqueous medium. The presence of a sulfoxide group in the DMSO molecule accounts for the unusual behavior of H/D-isotopes of water in DMSO medium compared to their standard solutions in amides.

The D_2O-H_2O-isotope effects (IEs) in the standard molar enthalpy of water solvation have been found to correlate quite correctly with the hydrogen bonding energy of H_2O - aprotonic dipolar solvent. The indicated enthalpy-isotope effects of solvation generally correlate also with the half-sum of the donor and acceptor numbers (according to *Gutmann* [39]) for the compared aprotonic dipolar media. In addition, there is a functional relationship between the IE in the enthalpy of water solvation in amides and the "solvent structuring" parameter proposed by *Otaki* [66].

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