Short communication

Water as a solute in aprotic dipolar solvents. 1. D₂O–H₂O solute isotope effects on the enthalpy of water dissolution in acetone, tetrahydrofuran and 1,4-dioxane at 298.15 K

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ABSTRACT

The enthalpies of solution of H_2O and D_2O in tetrahydrofuran (THF), 1,4-dioxane (DO) and acetone (AC) were measured calorimetrically at 298.15 K. Standard (at the infinite dilution) enthalpies of solution, along with D_2O–H_2O solute isotope effects on the quantity in question, were calculated. The enthalpies of the solute dissolution were found to be positive by sign and decreasing in magnitude on going from DO to AC and THF, whereas the corresponding solute isotope effects change in a consequence THF > AC > DO. It was concluded that the enthalpic D_2O–H_2O effects of water dissolution (solvation) are connected with both the donor-accepting ability and structure-packing peculiarities of the aprotic dipolar solvents compared.

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1. Introduction

The dilute solution of water in an aprotic dipolar solvent is of great interest. The point is that such a solvent is the dissolving medium, whose structure packing contains molecules that do not form strong hydrogen bonds (due to the absence of proton-donating centers) but allows rather strong specific interactions (via H-bonding) with molecules of an electron-accepting protic solute, which in this case is water [1–4]. Besides, in such liquid systems the long range structure of water, which is so important to the properties of dilute aqueous solution, is no longer in existence, and the only species of any importance are monomers, dimers, etc. [3].

Over the last decade, we have seriously studied volumetric properties of binary solutions involving solvents such as acetonitrile (AN), hexamethylphosphoric triamide (HMPT), 1,4-dioxane (DO), acetone (AC), nitromethane (NM), etc. and water isotopologue (H_2O or D_2O) as a solute in a wide temperature range [1,2,5–9]. The results obtained clearly show that the H_2O–D_2O solute isotope substitution is a fine tool for analyzing structure-packing alterations (including hydrogen-bonding effects) induced by the presence of dissolved water molecules. Meanwhile, some questions concerning both the energy-related state of water in the media considered and

peculiarities of the solute interaction with solvation environment still remain unanswered. Therefore in continuation of our work related to studies of solutions of water in aprotic dipolar media, we have now extended it to a number of such binary water-containing systems, using an experimental approach based on a combination of the solution calorimetry and H_2O–D_2O solute isotope substitution methods. Replacement of H_2O by D_2O in the given case is dictated by changing both the vibrational/translational motions and donor-accepting ability of water molecules that brings about the formation of deuterium bonds being stronger compared with the similar protium bonds [1,10,11].

We report in this paper, the calorimetrically measured enthalpies of solution of H_2O and D_2O in tetrahydrofuran (THF), DO and AC at 298.15 K. The choice of these aprotic dipolar solvents as the solvating media was made mainly for a reason of comparability of their donor-accepting properties (namely, the Gutmann's donor, DN_{SbCl_5}, and acceptor, AN, numbers for THF, DO and AC are 20.0, 14.8, 17.0 and 8.0, 10.8, 12.5, respectively [12]). Being the predominantly electron-donating media generally with low dielectric constants [13], the chosen solvents, however, differ noticeably from each other in structure-related properties. If THF (or oxolane) and DO consist of cyclic molecules with one and two oxygen heteroatoms in the cycle, respectively, AC being the simplest ketone is formed by means of molecules with an oxygen carbonyl-atom. On the other hand, THF and AC are "loosely packed" liquids with the similarly low heats of vaporization, $\Delta_{vap}H°$ [14].

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Table 1
Sources, purities, densities (ρ, g cm^{-1}) and refractive indexes (n_D) of solvents used at 298.15 K.

Solvent	Source	Initial purity[a]	Water content[a,b]	ρ		n_D	
				Expt.	Literature	Expt.	Literature [14]
THF	Fluka	≥99.9	≤0.006	0.88203	0.882056[c], 0.88208[d]	1.4048	1.4050
DO	Merck	≥99.5	≤0.006	1.02812	1.028337[c], 1.02797[e]	1.4202	1.4203
AC	Fluka	≥99.9	≤0.004	0.78465	0.78455[f], 0.784701[g]	1.3563	1.3560

[a] In wt%.
[b] After purification.
[c] Ref. [3].
[d] Ref. [19].
[e] Ref. [20].
[f] Ref. [21].
[g] Ref. [22].

To the best of our knowledge, at present there exist some calorimetrically obtained data on the standard enthalpies of solution, $\Delta_{sol}H^\infty$, and solvation, $\Delta_{solv}H^\circ$, for ordinary water in the compared solvents at $T = 298.15$ K [1,15–18]. Herewith we are aware only one study [17] describing the results of determination of $\Delta_{sol}H^\infty$ ($\Delta_{solv}H^\circ$) for heavy water in DO. However, it should be taken into account that, substituting H_2O by D_2O in the cases in question, it is important to use the solutes of the same (high) quality and to carry out the calorimetric measurements under the same conditions.

2. Experimental

Water was distilled from an alkaline solution of $KMnO_4$ and then redistilled in a quartz still to reach the electric conductivity $\kappa \approx 1.3 \times 10^{-6}$ S cm^{-1}. Heavy water D_2O (Izotop Co., St. Petersburg; $\kappa \approx 1.0 \times 10^{-6}$ S cm^{-1}) with natural ^{18}O-content and deuterium content being (99.95 ± 0.02) at.% D was used as such.

Characterization data for solvents under study are listed in Table 1. DO and THF were kept several days over KOH, refluxed for 24 h, fractionally distilled over metal sodium under an atmosphere pressure (at the presence of gaseous N_2), and the middle fraction collected and treated with 0.3-nm molecular sieves for several days. AC was simply distilled under dried nitrogen, and the middle fraction of distillate was kept over molecular sieves (0.3-nm) for several days too. Each solvent sample was distilled immediately before use. The first and the last fraction were discarded. The water content of these liquids (see Table 1) was determined with a Karl Fischer titration. Purity of each solvent was checked by measuring the density and refractive index at 298.15 K. Densities (ρ) were measured using a vibrating-tube densimeter DMA 4500 with an accuracy of $\pm(1.5 \times 10^{-5})$ g cm^{-3}. Refractive indexes (n_D) were measured with a Pulfrich refractometer (PR 2). The accuracy of n_D measured is

on the order of ± 0.0001. Table 1 shows that our results are in good agreement with values obtained from the literature sources. All the solvents were stored in dark glass bottles under air-tight conditions.

The experimental enthalpies of solution of water isotopologues, $\Delta_{sol}H^m$ (m is the solution molality), in the aprotic dipolar media studied were measured at (298.15 ± 0.005) K using an automated isoperibol (ampoule-type) calorimeter fitted with a 60 cm^3 reaction titanium vessel and electrical calibration (before each experiment). The detection limit of the apparatus is 10 μK. Correction to the presence of solute vapor in incompletely filled ampoules was taken into account at calculations. The relative random error of measurements did not exceed 0.5%. The calorimeter setup and experimental procedure were detailed previously [23].

3. Results

The calorimetric measurements showed that the $\Delta_{sol}H^m$ values in the high dilution region do not depend (within the experimental error) on m those ranging between 0.08 and 0.21 mol of H_2O and between 0.04 per 0.17 mol of D_2O per 1 kg of the solvent. Therefore, the $\Delta_{sol}H^\infty$ values (*i.e.*, the molar enthalpies of water dissolution at infinite dilution) have been calculated as average values $|\Delta_{sol}H^m|_{av}$ over five concentration-dependent measurements, according to the procedure described previously [23,24]. The experimental data on $\Delta_{sol}H^\infty$ for H_2O and D_2O in the aprotic dipolar solvents in question are listed in Table 2 together with the results existing in literature.

As can be seen from data of Table 2, the $\Delta_{sol}H^\infty$ values for solute water at 298.15 K are in very good agreement with our own, excepting quantities for H_2O and D_2O in DO reported by Duer and Bertrand [17]. Their enthalpic effects of water dissolution are more endothermic, differing from ours by *ca.* 0.2 kJ mol^{-1}. However, in the given

Table 2
Standard molar enthalpies of solution, $\Delta_{sol}H^\infty$ (kJ mol^{-1}), and solvation, $\Delta_{solv}H^\circ$ (kJ mol^{-1})[a], of ordinary and heavy water in tetrahydrofuran, 1,4-dioxane and acetone at 298.15 K.

Solvent	Solute H_2O		Solute D_2O		Isotope effect (D_2O–H_2O)–	
	$\Delta_{sol}H^\infty$	$-\Delta_{solv}H^\circ$	$\Delta_{sol}H^\infty$	$-\Delta_{solv}H^\circ$	$\delta\Delta_{sol}H^\infty$	$-\delta\Delta_{solv}H^\circ$
THF	4.28 ± 0.04	39.73 ± 0.04	4.84 ± 0.02	40.55 ± 0.02	0.56 ± 0.05	0.82 ± 0.05
	4.36 ± 0.03[b]	39.65 ± 0.03[b]				
DO	6.09 ± 0.04	37.92 ± 0.04	6.47 ± 0.02	38.92 ± 0.02	0.38 ± 0.05	1.00 ± 0.05
	6.08 ± 0.17[b]	37.93 ± 0.17[b]				
	6.29 ± 0.02[c]	37.72 ± 0.02[c]	6.62 ± 0.02[c]	38.77 ± 0.02[c]	0.33 ± 0.03[c]	1.05 ± 0.03[c]
AC	4.33 ± 0.05	39.68 ± 0.05	4.76 ± 0.04	40.63 ± 0.04	0.43 ± 0.06	0.95 ± 0.06
	4.39 ± 0.05[d]	39.62 ± 0.05[d]				

[a] Standard enthalpies of H_2O and D_2O vaporization, $\Delta_{vap}H^\circ$ (298.15 K), are 44.007 and 45.392 kJ mol^{-1}, respectively [1,10].
[b] Ref. [16].
[c] Ref. [17].
[d] Ref. [18].

case, the D_2O–H_2O solute isotope effects (hereinafter, IEs or δ) on $\Delta_{sol}H^\infty$ are found to be close to each other (Table 2).

4. Discussion

As it have been mentioned in Section 1, the calorimetry measurements are helpful in developing the present knowledge of solvation of water molecules and their interactions with the surroundings. This is particularly true when enthalpic effects of dissolution and solvation are combined with the corresponding D_2O–H_2O solute IEs because the latters are dominated by changes in the hydrogen-bonding between interacting like or unlike molecules.

According to the data in Table 2, the dissolution of water isotopologues in all the aprotic dipolar media in question is the endothermic process that becomes more pronounced on going from AC and THF to DO. Herewith the positive (in sign) D_2O–H_2O solute IEs on the quantity considered undergo changes in a consequence THF > AC > DO. Such a behavior of $\Delta_{sol}H^\infty$ and $\delta\Delta_{sol}H^\infty$ ($H_2O \rightarrow D_2O$) values gives us the certain information about the different strengths in the solute–solvent interactions.

A positive sign at the $\Delta_{sol}H^\infty$ ($=\Delta_{solv}H^\circ - \Delta_{vap}H^\circ$) value suggests that the solute–solvent interaction is weaker than the interaction between molecules in their own liquid medium of H_2O or D_2O. Indeed, taking into account that $\Delta_{vap}H^\circ = \Delta_{cond}H^\circ$ (where $\Delta_{cond}H^\circ$ is the standard enthalpy of solute condensation), the sign and magnitude of $\Delta_{sol}H^\infty$ are determined by the difference between solute–solvent and solute–solute interactions, because the solvation of a solute can be identified with the condensation of one mole of its gaseous molecules in an infinitely large amount of a solvent [16,25]. Hence the main contributions in $(\delta)\Delta_{sol}H^\infty$ are two enthalpic effects connected with the energy expenditure at creating the solvation cavity in a solvent (a positive contribution) and the heat evolution at associating the ordinary or heavy water with a surrounding solvent generally through hydrogen-bonding and non-specific interactions (a negative contribution).

Considering in this light the above-noticed interaction properties of solvents and enthalpy effects of solution of water isotopologues (see Table 2) jointly, one may conclude that there is an obvious interrelation between values of DN_{SbCl_5} for the pure AC, THF and DO and $\delta\Delta_{sol}H^\infty$ ($H_2O \rightarrow D_2O$) for the water in these aprotic dipolar media. As can be seen in Fig. 1, such interrelation is a close-to-linear function that can be regarded as an argument in favor of the belief that the energy-related changes due to solute–solvent and solvent–solvent interactions are manifested to a larger extent in the infinitely dilute solution of water in THF. The given conclusion is in agreement with the results of some works devoted to studying the compared water-containing media by both thermodynamic [3,26,27] and spectroscopic [28] methods. Hence, observed from the data of Table 2, the tendency to an increase in the endothermicity of dissolution of water within the series THF ≤ AC < DO can be explained generally by a decrease in the proton-donor capacity or acidity of the solvent (see Fig. 1).

Most interesting, however, is the fact that the $\Delta_{sol}H^\infty$ values for H_2O and D_2O in AC and THF are materially equal (within the limits of experimental accuracy, in Table 2) although the solute molecules interact in a different way with surrounding molecules of solvents compared. We are inclined to believe that this situation is most likely due to mutual imposing the several enthalpic effects that first of all are caused by weakening the steric hindrances for the solute–solvent interactions through H-bonding (and van der Waals contacts as well). One can suggest that the "parent" structure matrix of AC should be best suited for incorporating into them a H_2O and, especially, D_2O molecule, reducing the energy expenditure at creating of the solvation cavities and revealing the presence
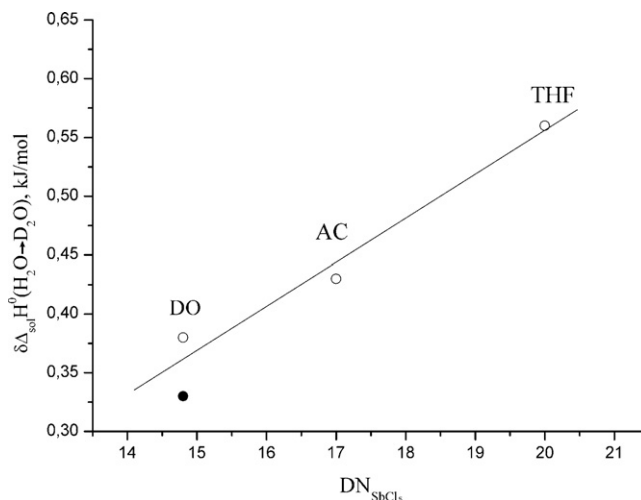

Fig. 1. The correlation between D_2O–H_2O solute isotope effects on the standard molar enthalpy of water dissolution in the aprotic dipolar solvents compared and Gutmann's donor numbers peculiar to the dissolving medium at 298.15 K: (○) our data; (●) value taken from Ref. [17]. (The values of half-width of confidence interval for the enthalpy-isotope characteristics under consideration are presented in Table 2.)

of additional steric incompatibilities when the specified solutes are solvated by the cycloetheres studied.

In conclusion, it should be noted that the $\Delta_{sol}H^\infty$ and $\delta\Delta_{sol}H^\infty$ ($H_2O \rightarrow D_2O$) values do not provide a complete information on the energy changes in the solvent structure induced by the solvation of water molecules. To compare the solvation enthalpic effects of two isotopically distinguishable solutes in question, the energy spent to destroy the structure packing of each of them (i.e., the $\Delta_{vap}H^\circ$ values) must be taken into account. The analysis of data in Table 2, referring to the enthalpy–solvation characteristics leads us to the following. Firstly, it is clear that water isotopologues in THF and AC are solvated the stronger than in DO, emphasizing a correctness of the above-made findings. Secondly, in all the cases considered, the change in $\Delta_{solv}H^\circ$ caused by a deuteration of water molecules points to strengthening the solute solvation that can be considered as a corroboration of the presence of "specific" interactions between the solute and solvent molecules. Thirdly, noteworthy is that the D_2O–H_2O solute IEs on $\Delta_{solv}H^\circ$ as a whole are roughly equal to the IE on the energy of water–water hydrogen bond, which amounts to $-(1.0 \pm 0.1)$ kJ mol^{-1} at 298.15 K [10,29]. This indicates the molecules of water isotopologues are really capable of forming the rather strong hydrogen (H- or D-) bonds in aprotic dipolar media in question. Finally, referring to the data of Table 2, it is seen that D_2O–H_2O solute IEs on $\Delta_{solv}H^\circ$ for solutions of water in DO and AC are close to each other, exceeding the similar value for the system (THF + water) in magnitude. It is interesting that, unlike the above-mentioned distribution of $\delta\Delta_{sol}H^\infty$ ($H_2O \rightarrow D_2O$), the enthalpy–isotope characteristic of water solvation changes generally as a function of the electron-accepting ability of a solvent.

According to conclusions [30], such an unusual solvation behavior for water in DO may be explained by formation of different hydrogen-bonded (cluster-like) structures in the two H/D isotopically distinguishable systems compared, but the surprisingly close to each other values of $\delta\Delta_{solv}H^\circ$ ($H_2O \rightarrow D_2O$) for water in DO and AC is not yet subject to a reasonable explanation. Unfortunately, the available data do not allow an analysis of this phenomenon in more details.

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