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Solubility and Thermodynamics of Solvation of Krypton in Mixtures of H/D Isotopomers of Water and Methanol at 101325 Pa and 278–318 K

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Abstract—The solubility of krypton in mixtures of H/D isotopomers of water (H_2O, D_2O) and methanol (CH_3OH, CD_3OH, CH_3OD) was studied at 101325 Pa and 278.15–318.15 K with a 10 K step. The thermodynamic characteristics of Kr solvation were calculated. The densities of mixtures of water and methanol isotopomers at the examined temperatures were calculated with an error of no more than 1×10^{-5} g cm^{-3} in the entire composition range. Both in water and aqueous methanol, krypton behaves as a structure-making component, but the alcohol solvation surrounding of the Kr atoms is more labile and more susceptible to the breaking effect of temperature.

Replacement of protons by deuterons in molecules of components of a liquid-phase system is a fine effect which, however, sometimes gives rise to relatively large isotope effects in physicochemical properties of the solvent and solution [1–3].

The thermodynamic characteristics of isotope effects and solvation reflect on the macroscopic level the structural differences between the H/D isotopomers of the solvent both in the pure form and in solution. These differences arise from the differences in the vibrational properties of molecules (vibrational contribution), in their size, and in the capability for intermolecular hydrogen (or deuterium) bonding (configurational contribution) [1–4].

The isotopic difference in the vibration (or libration) energy results in the electron density redistribution and hence affects the capability for hydrogen bonding, either by enhancing the electron-acceptor power (or weakening electron-donor power) in going from H_2O to D_2O or from CH_3OH to CH_3OD, or by enhancing the electron-donor power (or weakening electron-acceptor power) in going from CH_3OH to CD_3OH [5]. Consideration of these changes simplifies and makes more adequate the interpretation of the thermodynamic macroproperties of a protonated system.

Our previous studies [6–8] demonstrate the efficiency of this approach in studying structural features of methanol–water mixtures. In that studies, we considered the isotope effects in the bulk properties, related to replacement of one binary system by another and to transfer of 1 mol of methanol to water or of 1 mol of water to methanol. When deuteration of the groups forming H bonds was considered, the isotope substitution took place in both solvent and solute molecules.

Additional information about the structural state of water–methanol mixtures can be obtained by measuring the solubilities of nonpolar gases in such mixtures. As shown in [3, 9–12], molecules (or atoms) of a nonpolar (noble) gas introduced into a solution, owing to their hydrophobic hydration [13], act as probes sensitive to structural changes that occur in water or mixed aqueous-organic solvents with a low content of a nonaqueous component on changing temperature, pressure, or solution composition.

In this work we measured the solubility and calculated the standard thermodynamic functions of solvation $\Delta_{\mathrm{solv}}Y^0_{\mathrm{A}}$ (subscript A refers to the gas) of Kr in mixtures of H/D isotopomers of water and methanol: H_2O–CH_3OH (L_H), H_2O–CD_3OH (L_{1D_3}), and D_2O–CH_3OD (L_{D_1}). The measurements were made at 278.15, 288.15, 298.15, 308.15, and 318.15 K over the entire range of compositions of the mixed water–methanol solvent. We also accurately measured the densities of these systems.

Isotope effects in solubility. The Kr solubility data are given in Table 1 in the form of Bunsen absorption coefficients β^*_{A}. The procedure for determining β^*_{A}

Table 1. Solubility of Kr [β^*_A, cm^3 gas (dm^{-3} solvent)] at 101 325 Pa in water–methanol mixtures L differing in the H/D isotopic composition

L	T, K	Mole fraction of alcohol X_2					
		0	0.06	0.1	0.3	0.6	1.0
L_H	278.15	93.65	101.93	100.10	119.12	271.06	622.7
	288.15	70.64	79.42	81.38	109.18	259.49	579.4
	298.15	55.81	64.86	69.21	102.19	249.30	540.2
	308.15	45.91	55.10	61.07	97.57	240.65	505.0
	318.15	39.22	48.57	55.63	94.55	232.98	473.9
L_{1D_3}	278.15	93.65	102.05	100.06	119.38	272.26	626.4
	288.15	70.64	79.48	81.26	109.23	259.94	581.3
	298.15	55.81	64.89	69.05	102.17	249.21	540.4
	308.15	45.91	55.08	60.86	97.37	240.14	503.7
	318.15	39.22	48.55	55.48	94.32	232.08	470.8
L_{D_1}	278.15	102.48	109.72	107.33	122.62	278.14	637.1
	288.15	76.57	84.66	86.28	111.76	265.43	591.4
	298.15	60.16	68.60	72.75	104.23	254.30	549.9
	308.15	49.22	57.96	63.77	99.14	244.69	512.5
	318.15	42.06	50.92	57.88	95.90	236.43	479.2

was described in detail in [14], and the main calculation expressions are given in Experimental.[1]

A comprehensive analysis of the possibilities and consequences of using various concentration scales in thermodynamics of solutions [3] showed that, in calculation of the thermodynamic functions of transfer, including isotope effects, it is neccessary to use unitary concentrations (rational concentration scales) such as, e.g., the solvomolality scale c_{sm} [3, 16, 17]. Application of this scale to calculation of thermodynamic functions will keep constant the ratio of the number of dissolved gas molecules to the number of solvent molecules in going from one mixture composition to another and will eliminate the so-called cratic contribution originating from different molar weights and densities of solvents.

The parameter β^*_A was recalculated to the $c_{sm,A}$ scale by the formula

$$c_{sm,A} = (55.50843 M^*_L \beta^*_A)/(V^*_{n,A}\rho^*_L), \qquad (1)$$

where $M^*_L = X_1M^*_1 + X_2M^*_2$ and ρ^*_L are, respectively, the mean molecular weight (taking into account the degree of deuteration of the components) and density of the solvent (L_H or L_D), and $V^*_{n,A}$ 22 388 cm^3 mol^{-1} [18] is the actual molar volume of Kr under normal conditions. The normalizing factor of 55.50843 is numerically equal to the amount of H_2O (mol) in 1 kg of water. The densities of the mixtures are given in Table 2.

Figure 1 shows the isotope effects in the solubility of Kr, $\Delta_{tr}c_{sm,A}(L_H \to L_D)$, which were calculated as the differences between the $c_{sm,A}$ values in the deuterated and protonated solvents.

It is known that aqueous solutions of nonpolar gases are not characterized by strong interactions with the surrounding solvent molecules. The hydrophobic nature of hydration of spherically symmetrical gas atoms is due to predominant arrangement of these atoms in the areas of the ordered structure characteristic of water isotopomers. As a result, the extent of H bonding in the hydration surrounding grows [3, 9, 20–22]. The promotion of the water structure upon introduction of Kr atoms in manifested the stronger, the more structured is the solvent. This results in the growth of the gas solubility in going from naturally abundant water (or L_H mixture) to heavy water (or L_{D_1} mixture), or with decreasing temperature (Table 1, Fig. 1).

As the mean energy of deuterium bonds is higher, the tendency of the solvent to preserve the structure characteristic of pure water results in stronger correla-

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[1] The choice of this form of data presentation was governed by the experimental conditions which do not involve measurement of the partial gas pressure $\bar{p}_A$. The coefficient β^*_A is independent of $\bar{p}_A$ by definition and is always related to $\bar{p}_A$ 101 325 Pa.

Table 2. Density (ρ^*_L, g cm^{-3}) of mixtures of H/D isotopomers of water and methanol[a]

L	T, K	Mole fraction of alcohol X_2					
		0[b]	0.06	0.1	0.3	0.6	1.0
L_H	278.15	0.999964	0.98374	0.97556	0.93765	0.87651	0.80516
	288.15	0.999101	0.98224	0.97324	0.93169	0.86852	0.79579
	298.15	0.997047	0.97967	0.96993	0.92528	0.86034	0.78636
	308.15	0.994035	0.97617	0.96582	0.91854	0.85196	0.77688
	318.15	0.990216	0.97173	0.96104	0.91141	0.84336	0.76735
L_{1D_3}	278.15	0.999964	0.99359	0.99141	0.97776	0.93999	0.88510
	288.15	0.999101	0.99207	0.98900	0.97152	0.93144	0.87467
	298.15	0.997047	0.98946	0.98568	0.96490	0.92270	0.86420
	308.15	0.994035	0.98597	0.98153	0.95788	0.91373	0.85368
	318.15	0.990216	0.98163	0.97665	0.95041	0.90445	0.84311
L_{D_1}	278.15	1.10546	1.08070	1.06758	1.00789	0.92200	0.82893
	288.15	1.10571	1.07990	1.06556	1.00147	0.91361	0.81921
	298.15	1.10430	1.07770	1.06246	0.99474	0.90504	0.80946
	308.15	1.10159	1.07435	1.05836	0.98756	0.89624	0.79967
	318.15	1.09777	1.06993	1.05335	0.97990	0.88716	0.78983

[a] For each composition except X_2 0, the ρ^*_L values were determined by interpolation of the results of three independent measurements (at $\Delta X_2 \le \pm 0.001$). The $\rho^*_L(H_2O)$ and $\rho^*_L(D_2O)$ values are given in [19].

tion (and probably in increased number and/or multiplicity) of hydrogen bonds in heavy water [4]. An increase in the number of H bonds in water in the vicinity of krypton atoms and other large nonpolar particles was also confirmed by molecular-dynamics simulation in [23, 24].

According to the IR data [25], the tetrahedral ordering in the mutual arrangementg of oxygen atoms of molecules in the L_H system is preserved up to the methanol mole fraction X_2 ~0.3. It is commonly believed that this is the range of the highest structural stability, manifested, e.g., in the lowest concentrations of free OH groups and lowest self-diffusion coefficients of alcohol and water molecules [25]. According to Bushuev's estimates [26] based on Monte-Carlo simulation of the structures of L_H mixtures, the range of existence of an H-bond "subnetwork" built exclusively from water molecules extends to the mole fraction of the alcohol close to 0.4. At higher methanol concentrations, the common H-bond network disintegrates to chains of various lengths.

The trends in variation of $\Delta_{tr}c_{sm,A}(L_H \rightarrow L_D)$ in the examined range of compositions ($0 \le X_2 \le 0.3$) of water–methanol solvents confirm and supplement the above-given data. The isotope effect in the solubility of Kr upon the replacement $L_H \rightarrow L_{D_1}$ decreases with increasing content of methanol and passes through a minimum at X_2 ~0.3. This result is consistent with the concept that the cooperative D-bond network in the L_{D_1} system is more correlated than in the L_H system. Therefore, the structure of the deuterated solvation complex is more susceptible to the breaking effect of methanol additions and temperature. The isotope ef-

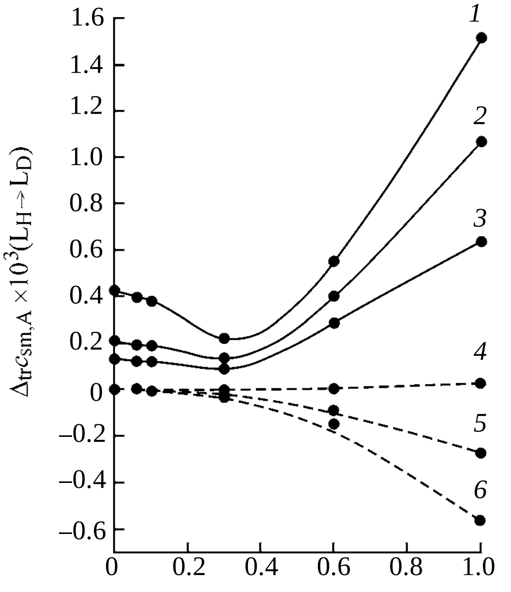

Fig. 1. Isotope effect in solubility of Kr in water–methanol mixtures as a function of solvent composition at various temperatures. Here and in Fig. 2, solid lines refer to the $L_H \rightarrow L_{D_1}$ substitution, and dashed lines, to the $L_H \rightarrow L_{1D_3}$ substitution. T, K: (*1*, *4*) 278.15, (*2*, *5*) 298.15, and (*3*, *6*) 318.15 K. The same for Fig. 2.

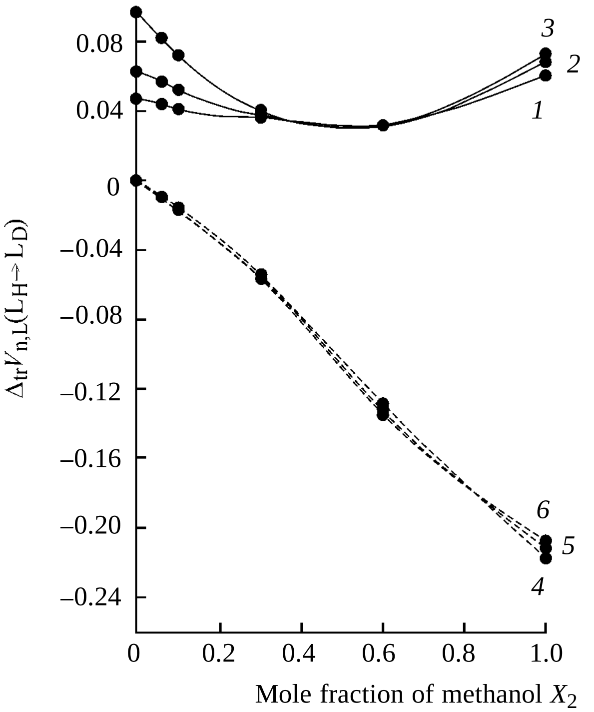

Fig. 2. Isotope effect in the molar volume of water–methanol mixtures as a function of their composition.

fects $\Delta_{tr}c_{sm,A}(L_H \rightarrow \Lambda_{1D_3})$ at $X_2 \leq 0.3$ are close to zero over the entire temperature range studied.

Such a behavior of the dependences $\Delta_{tr}c_{sm,A}(X_2, T)$ in the water-rich range of L_H compositions allows two important, in our opinion, conclusions. First, formation of solvation or hydration complexes is largely affected by configurational changes associated with the size, shape, and mutual arrangement (direction and length of H bonds) of molecules. Second, apparently, nonspecific (van der Waals) interactions between the water, alcohol, and gas molecules should not be considered as factors responsible for anomalies in the composition–property relationships.

These conclusions are confirmed by the composition dependences of the isotope effects in the molar volume of the system (Fig. 2). The $\Delta_{tr}V_n(L_H \rightarrow L_D)$ values were calculated from data in Table 2 and in [8]. It is noteworthy that the $\Delta_{tr}c_{sm,A}(X_2)$ (Fig. 1) and $\Delta_{tr}V_n(X_2)$ (Fig. 2) functions vary in parallel up to X_2 ~0.3, i.e., there is a clear correlation between the decreases in the Kr solubility and in the free (excluded) volume in the L_{D_1} system.

However, whereas the isotope effect in the molar volume of the mixed solvent at $X_2 > 0.3$ depends on temperature insignificantly (Fig. 2), the plots of $\Delta_{tr}c_{sm,A}(L_H \rightarrow L_D)$ at different temperatures form a fan-shaped pattern (Fig. 1). Such a behavior suggests manifestation not only of structural features of methanol isotopomers, but also of the effects of the gas solvation associated with differences in the vibrational (donor–acceptor) and configurational properties of the solvent.

In the range of X_2 up to ~0.3, the nature of the structural effects of solvation is determined, on the whole, by the topological properties of the H-bond network characteristic of pure water. At higher methanol concentrations in the L_H mixture, the major factors governing the structural and energetic characteristics of solvation are, apparently, formation of mixed (“homo- and heterocomponent”) H-bonded chains of water and methanol molecules and mutual packing of the methyl groups [26]. However, such a “demarcation” is largely conventional; it does not reflect specific features of transient structural states in the range of alcohol-rich compositions.

Replacement of protons by deuterons in the methyl group causes a more substantial, compared to the $CH_3OH \rightarrow CH_3OD$ replacement, decrease in the size and polarizability (zero vibration frequencies) of the methanol molecules [1]. The molar volume of methanol decreases (Fig. 2). Presumably, the lack of the isotope effect $\Delta_{tr}c_{sm,A}(L_H \rightarrow L_{1D_3}$, 278 K) in the alcohol-rich composition range is due to compensation of the partial loss of the free volume (configurational changes) in the solvent matrix by strengthening of the alcohol–gas interactions. With increasing temperature, the isotope difference in the zero vibration energies of the L_H and L_{1D_3} molecules decreases faster than the isotope difference in the hydrogen bond energies. This, apparently, results in the growing negative isotope effect in the Kr solubility.

Thermodynamics of isotope effects of solvation. The thermodynamic characteristics of Kr solvation $\Delta_{solv}Y^0_A(L)$ were calculated by the procedure described in [27] and based on physically substantiated model (2) adequately reproducing the temperature dependence of the solubility of a gas that is chemically inert toward the medium.

$$R\ln c_{sm,A} = a_0 + a_1u_1 + a_2u_2. \qquad (2)$$

Here, $u_1 = (T - \theta)/T$, $u_2 = \theta/T + \ln(T/\theta) - 1$, and θ is a temperature arbitrarily chosen within the measurement range. The coefficients of Eq. (2) are mutually independent and correspond in the physical sense to the standard molar thermodynamic functions of solution (or solvation) of a gas at a temperature θ: $a_0 = -\Delta_{solv}G^0_A(\theta)/\theta$, $a_1 = \Delta_{solv}H^\infty_A(\theta)/\theta$, $a_0 + a_1 = \Delta_{solv}S^0_A(\theta)$, and $a_2 = \Delta_{solv}C^{\times}_{p,A}$. The $\Delta_{solv}H^\infty_A$ values calculated by this procedure are listed in Table 3. Figures 3 and 4

Table 3. Standard molar enthalpies of Kr solvation $\Delta_{solv}H^{\infty}_{A}(L)$ in water–methanol mixtures of various H/D isotope compositions

L	T, K	Mole fraction of alcohol X_2					
		0	0.06	0.1	0.3	0.6	1.0
L_H	278.15	19.79 ± 0.14	17.59 ± 0.06	14.61 ± 0.14	5.95 ± 0.07	2.42 ± 0.04	4.03 ± 0.07
	288.15	17.74 ± 0.08	15.40 ± 0.03	12.47 ± 0.08	4.79 ± 0.04	2.24 ± 0.02	4.09 ± 0.04
	298.15	15.69 ± 0.04	13.22 ± 0.02	10.33 ± 0.04	3.62 ± 0.02	2.06 ± 0.01	4.15 ± 0.02
	308.15	13.64 ± 0.09	11.03 ± 0.04	8.18 ± 0.09	2.45 ± 0.04	1.87 ± 0.03	4.21 ± 0.05
	318.15	11.59 ± 0.15	8.84 ± 0.06	6.04 ± 0.16	1.28 ± 0.08	1.69 ± 0.04	4.27 ± 0.08
L_{1D_3}	278.15	19.79 ± 0.14	17.62 ± 0.08	14.69 ± 0.11	6.06 ± 0.03	2.58 ± 0.05	4.18 ± 0.06
	288.15	17.74 ± 0.08	15.43 ± 0.04	12.54 ± 0.06	4.88 ± 0.02	2.40 ± 0.02	4.28 ± 0.03
	298.15	15.69 ± 0.04	13.25 ± 0.02	10.38 ± 0.03	3.71 ± 0.01	2.22 ± 0.01	4.37 ± 0.02
	308.15	13.64 ± 0.09	11.06 ± 0.05	8.23 ± 0.07	2.53 ± 0.02	2.04 ± 0.03	4.47 ± 0.04
	318.15	11.59 ± 0.15	8.87 ± 0.09	6.08 ± 0.12	1.35 ± 0.03	1.85 ± 0.05	4.56 ± 0.07
L_{D_1}	278.15	20.49 ± 0.15	18.37 ± 0.07	15.48 ± 0.11	6.35 ± 0.03	2.63 ± 0.05	4.16 ± 0.07
	288.15	18.30 ± 0.08	16.05 ± 0.04	13.19 ± 0.06	5.12 ± 0.01	2.45 ± 0.03	4.26 ± 0.04
	298.15	16.11 ± 0.04	13.73 ± 0.02	11.90 ± 0.03	3.89 ± 0.01	2.27 ± 0.02	4.36 ± 0.02
	308.15	13.93 ± 0.09	11.41 ± 0.05	8.60 ± 0.07	2.66 ± 0.02	2.09 ± 0.03	4.46 ± 0.04
	318.15	11.74 ± 0.16	9.09 ± 0.08	6.30 ± 0.12	1.44 ± 0.03	1.91 ± 0.06	4.56 ± 0.08

show how the temperature and solvent composition affect the transfer functions (isotope effects) $\Delta_{tr}\Delta_{solv}S^{0}_{A}(L_H \to L_D)$. These data show that the isotope effects $\Delta_{tr}\Delta_{solv}S^{0}_{A}(L_H \to L_D)$ and $\Delta_{tr}\Delta_{solv}H^{\infty}_{A}(L_H \to L_D)$ are negative at any methanol concentrations and temperatures. However, their behavior largely depends on the deuteration position in the methanol molecule. The isotope effects in $\Delta_{solv}S^{0}_{A}$ and $\Delta_{solv}H^{\infty}_{A}$ decrease with increasing temperature in the case of the $L_H \to L_{D_1}$ substitution and increase in the case of the $L_H \to L_{1D_3}$ substitution.

According to the model developed in [3, 10], the isotope effect in the entropy of solvation of a noble gas can be presented as a sum of two terms:

$$\Delta_{tr}\Delta_{solv}S^{0}_{A}(L_H \to L_D) = \Delta_{tr}\Delta S^{0}_{\mathbf{I},A}(L_H \to L_D) + \Delta_{tr}\Delta S^{0}_{\mathbf{II},A}(L_H \to L_D). \quad (3)$$

The first term corresponds to the isotope effect in the entropy of transfer of the gas molecules from the gas phase to the condensed medium of the solvent. The second term consists of at least two contributions. The first contribution is determined by the difference between the vibration frequencies (energies) in the molecular packings of the solvation shells of nonpolar gas atoms in L_H and L_D. The second contribution reflects the differences between the H/D-bond networks in the mixtures or individual solvent, and also the differences in the effect of the dissolved gas molecules on the structure of these networks.

The calculations made in [3, 12] showed that the contribution $\Delta_{tr}\Delta S^{0}_{\mathbf{I},A}(L_H \to L_D)$ is virtually independent of the solvent and nonpolar gas, and also of temperature, i.e., $\Delta_{tr}\Delta S^{0}_{\mathbf{I},A}(L_H \to L_D) \cong \Delta_{tr}\Delta_{solv}S^{0}_{A}(L_H \to L_D)$. In this connection, the negative values of $\Delta_{tr}\Delta_{solv}S^{0}_{A}(H_2O \to D_2O)$ and $\Delta_{tr}\Delta_{solv}H^{\infty}_{A}(H_2O \to D_2O)$ support the Zichi and Rossky's conclusion [4] based on molecular-dynamics simulation of solutions of Lennard–Jones particles in H_2O and D_2O that the zero vibration frequencies of the solvent molecules in the vicinity of gas particles appreciably decrease upon deuteration. In other words, the hydration shell of Kr consisting of D_2O molecules is more stable.

An increase in the temperature makes a small positive contribution to the vibrational component of the isotope effect. The major influence on the temperature dependence of the isotope effect $\Delta_{tr}\Delta_{solv}Y^{0}_{A}$ is exerted by the thermal breakdown of the H-bond network. This perturbing effect is more pronounced in more structured heavy water (or in D_2O-rich L_{D_1} mixtures) and in solvation shells around Kr atoms.

Considering from this viewpoint the effect of methanol additions on the thermodynamic characteristics of Kr solvation in water-rich L_H mixtures ($0 < X_2 < 0.3$), we can conclude that, at $X_2 < 0.1$, methanol molecules counteract the structure-breaking effect of temperature and, at $X_2 > 0.1$, enhance it. As seen from Fig. 3, the dependences of $\Delta_{tr}\Delta_{solv}S^{0}_{A}(L_H \to L_{D_1})$ on X_2 at low temperatures pass through a minimum. The

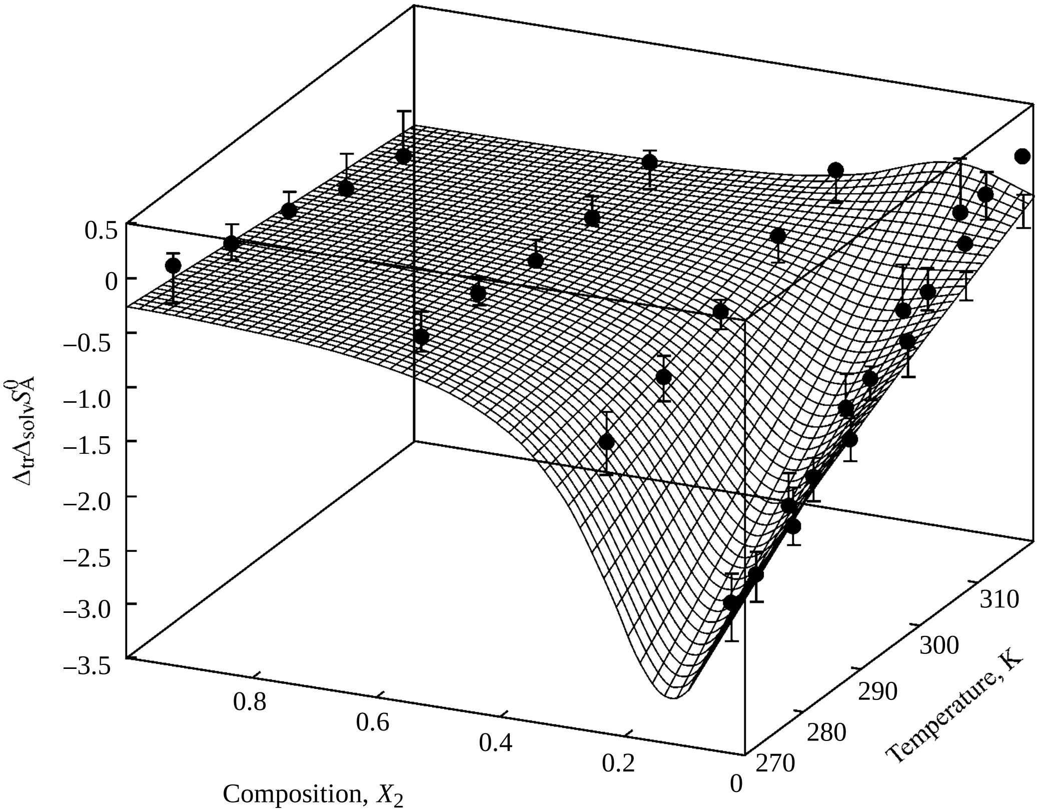

Fig. 3. Isotope effect in the entropy of solvation of Kr in the D_2O–CH_3OD mixture as a function of temperature and mixture composition.

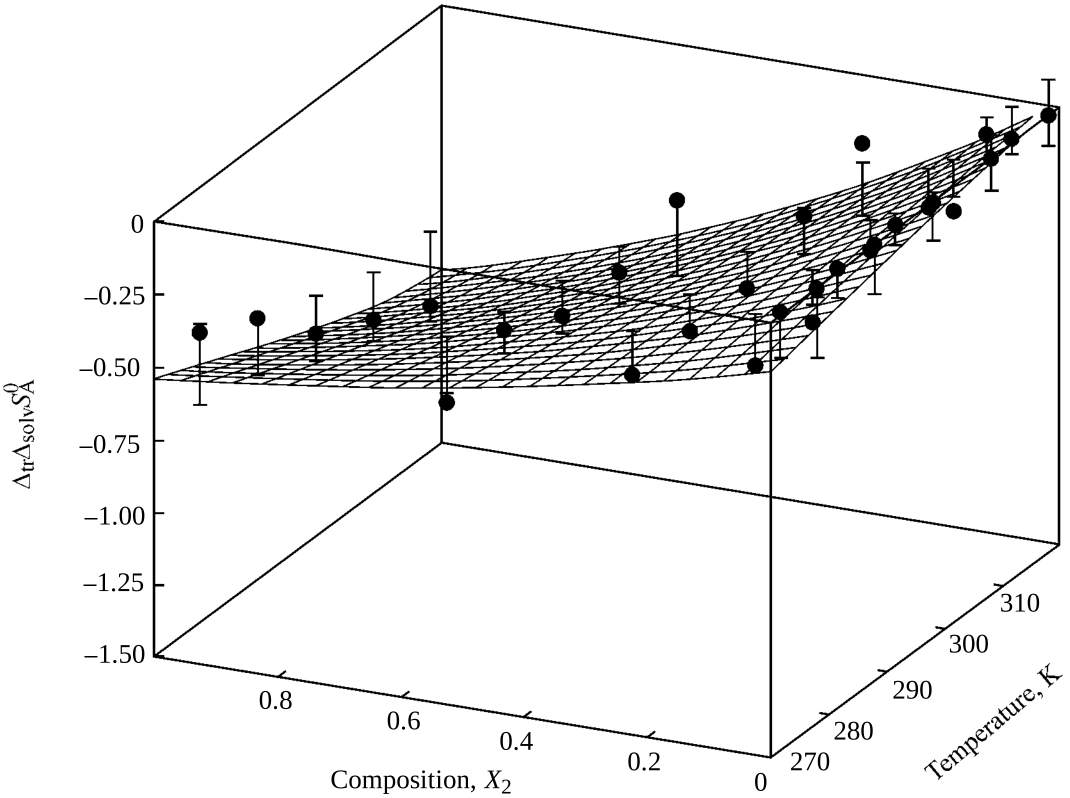

Fig. 4. Isotope effect in the entropy of solvation of Kr in the H_2O–CD_3OH mixture as a function of temperature and mixture composition.

isotherms $\Delta_{tr}\Delta_{solv}S^0_A(L_H \rightarrow L_{1D_3}, X_2)$ shown in Fig. 4 have no minimum. This difference may be due to the fact that, in formation of the alcohol–water solvation complex in the L_{D_1} system, the hydrophobic hydration of alcohol is more pronounced as compared to the protic system, whereas in the L_{1D_3} system it is less pronounced. A similar conclusion was made in [8] on the basis of isotope effects in the apparent molar volumes of alcohols: In L_{D_1}, these effects were negative with a minimum at X_2 ~0.1, whereas in L_{1D_3} they were positive with a maximum at the same composition.

The promotion of water structure with Kr atoms is enhanced by the stabilizing effect of the first additions of methanol. However, as the methanol mole fraction (at $X_2 > 0.1$) and temperature are increased, the differences between the structural properties of L_H and L_{D_1} systems gradually level out owing to the greater extent of correlation of the D-bond network and, correspondingly, to its higher sensitivity to external effects.

According to [26], in the L_H system at $X_2 \geq 0.3$, two types of topologically different equilibrium structures can be distinguished. In the subsystem consisting of water molecules, networks prevail. Methanol molecules, on the contrary, form chains consisting of a few monomers. Both subsystems are combined in a common network by heterocomponent H bonds and form a kind of a transient structural area. This conclusion is consistent with the trends in variation of the thermodynamic functions of krypton solvation, which pass through minima in L_H, L_{D_1}, and L_{1D_3} mixtures in the composition range $0.3 \leq X_2 \leq 0.6$, with the corresponding isotope effects being weakly temperature-dependent.

These data show that, in the systems in hand, Kr behaves as a structure-making agent, since its dissolution is accompanied by a significant decrease in the entropy, and the isotope effects $\Delta_{tr}\Delta_{solv}S^0_A$ and $\Delta_{tr}\Delta_{solv}H^\infty_A$ are negative. However, the water structure around the Kr atom is more ordered than the solvation structure in the methanolic solution. In other words, the solvation shell consisting of H-bonded methanol molecules is more labile and more susceptible to the breaking effect of temperature.

These distinctions are probably due to principally different nature of the solvation constituent in interaction of the gas with the surrounding methanol molecules. This is due not only to the absence of the common H-bond network in the alcohol, but also to the possibility of the van der Waals contact of the methyl group with the Kr atom. Therefore, the structural (solvophobic) effects of the gas solvation in methanol are, apparently, manifested to a considerably lesser extent than in aqueous solutions.

The isotope effects $\Delta_{tr}\Delta_{solv}S^0_A(CH_3OH \rightarrow CD_3OH)$ are negative at all the temperatures. This, apparently, supports the conclusions made in [5, 28–30] that replacement of CH_3OH by CD_3OH decreases the capability of the alcohol molecules for specific contacts, which, in turn, increases the relative contribution of the $\geqslant$C–H$\cdots$O< hydrogen bonding.

EXPERIMENTAL

Studies of H/D isotope effects in structural and thermodynamic properties of solvents require their especially thorough purification. Therefore, one of our main goals was to obtain samples with a very low content of impurities (mostly of residual moisture) and ensure their protection from the atmosphere.

In the experiments, we used ultrapure Kr (main substance content ≥99.9978 mol %. Water of natural isotope abundance was deionized in Wofatit ion-exchange columns and double-distilled in a device with quartz heaters; the first distillation was performed with addition of $KMnO_4$. The electrical conductivity æ of this water sample was ~1.3 μS cm^{-1}. Heavy water (æ ~1 μS cm^{-1}) was purchased from Izotop; its deuterium content, 99.83 ± 0.02 at. %, was determined by formula (4) [1].

$$X_D = 100(\rho_{1,X} - \rho^*_{1,H})/(\rho^{1}_{,D} - \rho^*_{1,H}). \quad (4)$$

Here, $\rho_{1,X}$ is the density of the heavy water sample; $\rho^*_{1,H}$ and $\rho^*_{1,D}$, the densities of H_2O (X_D ~0, Table 2) and D_2O (X_D 100 at. % [19, 31]). Chemically pure grade methanol (initial mole fraction of the main substance ≥0.9965) was additionally purified by refluxing over magnesium methylate followed by distillation [32]. The purity of the resulting CH_3OH samples, as evaluated from the density (using data of [7, 8]), by amperometric Fischer titration [33], and chromatographically, was ~0.9998 (on the mole fraction scale) after twofold dehydration. Deuterated methanols CD_3OH and CH_3OD (Izotop) had the deuterium content in the substituted positions of ~99.0 ± 0.1 at. % (as estimated from the integral intensities of the IR absorption bands) and the mole fraction of residual moisture (certificate data) of $\leq 1.5 \times 10^{-2}$. The deuterated methanols were purified as described above for CH_3OH, using a specially made microinstallation [34]. The H/D isotope exchange in the course of dehydration was excluded by preliminary evacuation of the installation, followed by filling with an inert gas. The purity of deuteromethanols was no worse than that of CH_3OH. The stability of the isotope composi-

Table 4. Comparison of data on the Kr solubility ($c_{\mathrm{sm,}} \times 10^3$) in H/D isotopomers of water and methanol at 101 325 Pa[a]

T, K	Kr–H_2O	Kr–D_2O	Kr–CH_3OH	Kr–CD_3OH	Kr–CH_3OD
278.15	4.187 [36]	4.611 [37][b]	59.07 [39][c]	61.91 [37][d]	63.47 [37][d]
	4.183 [38]	*4.602*	60.70 [41]	*61.466*	*62.954*
	4.182 [37]		61.20 [42]		
	4.183		*61.438*		
288.15	3.161 [36]	3.437 [37]	53.66 [39]	58.11 [37]	59.32 [37]
	3.157 [38]	3.438 [40][e]	57.31 [41]	*57.720*	*59.130*
	3.157 [37]	3.434 [43][e]	57.61 [42]		
	3.158	*3.438*	*57.839*		
298.15	2.508 [36]	2.703 [37]	53.96 [41]	54.18 [37]	55.79 [37]
	2.498 [38]	2.666 [40]	54.75 [42]	*54.306*	*55.646*
	2.499 [37]	*2.705*	*54.574*		
	2.500				
308.15	2.069 [36]	2.217 [37]	50.61 [41]	50.43 [37]	51.90 [37]
	2.061 [38]	2.218 [43]	51.52 [42]	*51.240*	*52.500*
	2.060 [37]	*2.218*	*51.645*		
	2.063				
318.15	1.777 [36]	1.903 [37]	47.03 [41]	46.81 [37]	48.06 [37]
	1.765 [38]	1.911 [43]	48.72 [42]	*48.503*	*49.701*
	1.765 [37]	*1.902*	*49.061*		
	1.769				

[a] The values obtained in this work are printed italic. [b] X_{D_1} 99.8 at. %. [c] Calculated from the equation $\ln X_A = -12.625 + 11.868/(T/100) + 1.4776 \ln (T/100)$ [39] for the range 173.15 K ≤ T ≤ 293.15 K, taking into account that $c_{\mathrm{sm,A}} = 55.50843 X_A/(1 - X_A)$. [d] $X_{1D_3} = X_{D_1}$ = 99.0 at. % [e] X_{D_1} ~100 at. %.

tion of alcohols was checked by comparing the densities (extrapolated to zero moisture content) of the initial and purified alcohols.

Water–methanol solutions were prepared gravimetrically from the degassed components in evacuated systems with an accuracy (on the mole fraction scale) of ~5×10^{-4}. The degassing procedure is described in detail in [35]. The weighing error did not exceed 5×10^{-5} g. The gas solubility was measured at the gas partial pressure of 101 325 Pa by the saturation technique on a precision microgasometric unit described in [14].

The Kr solubility (Bunsen absorption coefficients, β^*_A) was calculated by formula (5) (n.c. denotes normal conditions):

$$\begin{aligned}\beta^*_A(L) &= v_A(T,p)\text{–}273.15 z_A(\text{n.c})/[v_L(T,p) T z_A(T,p)] \\ &= v_A(\text{n.c}) z_A(\text{n.c})/[v_L(T,p) z_A(T,p)]. \qquad (5)\end{aligned}$$

Here v_A(n.c.) is the volume of the pure gas absorbed at experimental temperature T and pressure $p = p_{\mathrm{tot}}$ and recalculated to the partial pressure p_A 101 325 Pa and normal conditions (T^0 273.15 K, p^0 101 325 Pa); v_L is the volume of the degassed solvent at T and p_{tot}; z_A(n.c.) and $z_A(T,p)$ are the compressibility coefficients of the gas under normal conditions and at the experimental temperature and pressure, respectively, introduced to make corrections for the nonideal behavior. The z_A values were calculated by the Lee–Kessler method [15].

The accuracy of the measured β^*_A was checked by measuring the oxygen solubility in water, since the corresponding reference gasometric data are the most reliable and accurate. Repeated measurements of the $\beta^*_A(L_H, T)$ values demonstrated their good repeatability (~0.2%) and the absence of significant fixed errors. The random deviations did not exceed the attained accuracy of the solubility measurements (± 0.25%). To additionally check the reliability of our data on the Kr solubility in H/D isotopomers of water and methanol, we compared them with published data [36–43] (Table 4).

Table 4 shows that the $c_{\mathrm{sm,A}}$ values in H_2O and D_2O are nicely consistent. At the same time, data for the Kr solubility in methanol and its deuterated analogs are fairly consistent (except data of [39]) only for temperatures below 298 K. At $T > 298$ K, the difference between the $c_{\mathrm{sm,A}}$ values in methanol isotopomers reaches 5%. This may be due to differences in the purity of the alcohol and gas and in the procedures used to determine the solubility. It is necessary to take into account numerous factors that appreciably affect the amount of substance A absorbed in the course of dissolution in the bulk of substance L.

The density of solutions (Table 2) was determined by the magnetic flotation method on a hermetically sealed float densimeter [44] with an error no higher than 1×10^{-5} g cm^{-3}.

All the molar quantities were calculated using the IUPAC table of relative molecular weights of the year 1991 [45] [A_r(H) 1.00794, A_r(D) 2.01416, A_r(O) 15.99994, A_r(N) 14.00674, A_r(C) 12.01110 g mol^{-1}].

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