Volumetric properties of H_2O, D_2O, and methanol in acetonitrile at 278.15—318.15 K

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The densities of H_2O, D_2O, and MeOH solutions in acetonitrile with the solute concentrations up to 0.07 molar fractions at 278.15, 288.15, 298.15, 308.15, and 318.15 K were measured using vibrating-tube densimetry with an error $\leq 8 \cdot 10^{-6}$ g cm^{-3}. The limiting partial molar volumes for the H/D isotopomers of water and MeOH in acetonitrile ($\bar{V}_2^{\infty}$) and the isotope effects in $\bar{V}_2^{\infty}$ and in excess molar volumes of acetonitrile—water mixtures were calculated. Molecules of H_2O, D_2O, and MeOH form associates with acetonitrile molecules *via* hydrogen bonds. The associates have the packing volumes close to those in the individual solute. The water and methanol molecules were assumed to be incorporated into the acetonitrile structure without substantial changes in the latter. However, this process results in some compression of the system with a simultaneous increase in its expansibility.

Key words: water, acetonitrile, methanol, H/D isotope effects, limiting partial molar volumes, interparticle interactions.

The modern level of science and chemical technology development requires the ever growing application of nonaqueous individual and mixed solvents. At the same time, considering a nonaqueous solvent as one of the efficient facilities for controlling the chemical process, one should take into account that the absence or presence of traces of water in the solvent induces, in some cases, even stronger consequences than the replacement of the solvent.[1] Therefore, the study of the state and specific features of dissolved water in an organic solvent and the nature of their effect on the structure and thermodynamic properties of the dissolving medium is an important problem.

The behavior of water present in a very low content in a nonaqueous medium, where the three-dimensional network of H bonds characteristic of the "neat" aqueous component is absent, remains poorly studied until now. The results of studies performed in this area during two last decades (see, *e.g.*, Refs. 2—13) show that the properties of water dissolved in an organic solvent substantially depend on the nature of the latter. Researchers are interested most of all in such a dissolving medium, whose structural packing contains molecules that do not form strong H bonds (due to the absence of proton-donor centers) but allows a sufficiently strong specific interaction with molecules of an amphiprotic solute, which is water.

Acetonitrile (AN) plays an important role among similar aprotic dipolar solvents. This is determined by the fact that AN, on the one hand, is widely used in the petrochemical and food industry, pharmacology, and some other branches of industry and, on the other hand, it is the starting unit of the homological series of aliphatic nitriles and many compounds containing molecules with the nitrile (or cyanide) —C≡N groups.

Liquid AN in the individual state is a medium with a sufficiently high "electrostatic factor": $EF^* = \varepsilon^*\mu^* \approx$ 129 D* (for H_2O ~144 D).[14] The electron-donor ability of AN (according to Gutmann[15]) is lower than that of water: $DN_{SbCl_5} \approx 14.1$ kcal mol^{-1} (for H_2O ~18.0 kcal mol^{-1}).

The published data on the structural properties of AN are contradictory. Nevertheless, the authors of the most works[16—21] believe that molecules of this nitrile are capable of self-associating to form dimers, probably, due to the dipole-dipole and quadrupole-quadrupole interactions between the N and C atoms of the C≡N group of two adjacent molecules.

The present uncertainty in the interpretation of the structural features of AN affects the estimation of the character of the intermolecular AN—H_2O interaction. However, it is established that no structural microheterogeneity is observed in the structure of AN—H_2O mixtures at high (compared to the water content) dilutions.[12,22—25] Molecules of dissolved water form solvate complexes with the acetonitrile environment predomi-

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* The symbols marked with "asterisk" refer to the properties of an individual compound (solvent or solute).

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nantly due to either association through H bonds,[22—24] or strong dipole-dipole interactions.[25] At the same time, the formation of a strong H bond between the H_2O (or D_2O) molecule and N atom of the nitrile group is doubtful, because the N atom can presumably be involved in the formation of the C...N bond.[26] This is confirmed in part by the considerable endothermic effect of dissolution ($\Delta_{sol}H_2^\infty$) of H_2O in AN, which is[8] ~7.91 kJ mol^{-1} at 298 K.

Thus, the question about the forces resulting in the formation of the H_2O—AN structural aggregates in an infinitely (or strongly) dilute acetonitrile solution of water remains unanswered and, evidently, both spectroscopic[2,5,12] and other methods are needed to solve this problem. In addition to computer simulation, experimental methods developed according to the principle of minimum perturbation are useful: densimetry[27] and H/D isotope substitution.[28,29] A combination of these methods is especially efficient: densimetry provides a range of volumetric characteristics of a solution and its components, and H/D isotope substitution (due to the quantum nature of the isotope effect) allows one to establish at the molecular level the role of hydrogen bonds in effects of structurization, which are manifested in the volumetric and other properties.[7,10,11]

Therefore, we measured the densities of dilute solutions of the H/D isotopomers of water (H_2O and D_2O) in AN and calculated the volumetric characteristics of the solutes under study and the binary water-containing system as a whole in a wide temperature range. In addition, the volumetric properties of MeOH in AN were determined to reveal the specific features of the structural behavior of dissolved water for comparison.

Experimental

Procedure of experiments. Acetonitrile (reagent grade), which was twice dehydrated with phosphorus pentaoxide followed by distillation and collection of the medium fraction according to a previously described procedure,[30] was used. In order to remove P_2O_5 traces, the solvent was distilled over freshly calcined K_2CO_3 and subjected to fractional distillation without a drying reagent. The content of residual moisture determined by the Fischer method in purified AN was ~0.02 wt.%. Methanol (reagent grade) was additionally purified by a known method[30]: refluxing with magnesium methoxide followed by the distillation of the product to purity 0.99982 molar fractions (analysis by the Fischer method and densimetry). Deionized and twice distilled water with the natural isotope composition and heavy water D_2O (purchased from Izotop, Russia) with the deuterium content 99.83±0.01 at.% (based on density) and specific electric conductivity $\kappa \approx 1$ µS cm^{-1} were used to prepare solutions.

Solutions were prepared using the gravimetric method by diluting the degassed solvent. The composition of the solvent was expressed in units of the solvomolality concentration of the solute $c_{sm,2}$* and monitored with the accuracy to $3 \cdot 10^{-5}\ c_{sm,2}$.

Densities of solutions ρ_s were measured using a vibrating-tube densimeter, whose design and specific features have been described in detail elsewhere.[27,31] The error of ρ_s measurement (taking into account the influence of all possible factors) did not exceed $8 \cdot 10^{-6}$ g cm^{-3}. The total collection of the ρ_s values at the compositions and temperatures studied by us is published.[32]

The concentration dependence of the ρ_s values is adequately described by the approximating model

$$\rho_s = a_0(\equiv\rho_1^*) + a_2c_{sm,2}. \qquad (1)$$

The parameters of Eq. (1) are presented in Table 1. The most reliable (implying the accuracy of determination and comparability) published data on the density of AN chosen in the comparative analysis of the available experimental results are collected in Table 2. As can be seen from the data in Table 2, they agree well with our ρ_1* values.

Processing of experimental data. The data on ρ_s were used in calculations of the limiting partial molar volumes $\bar{V}_2^\infty$ and limiting partial molar expansibilities $\bar{E}_{p,2}^\infty$ of H_2O, D_2O, and MeOH in AN, as well as the excess molar volumes $V_{1,2}^E$ of the water-containing binary systems.

The rational (or "non-extrapolation") procedure[27,36] characterized by an elevated stability of the volumetric characteristic considered toward the effect of errors in the determination of the density and composition of the solution in the region of high dilutions was used for the estimation of $\bar{V}_2^\infty$. This method is based on the use of the volume of a binary solution V_s as the initial value. It is calculated using the formula

$$V_s = (n_1M_1^* + n_2M_2^*)/\rho_s. \qquad (2)$$

Here M_1* and M_2* are the molar weights of the components. In the solvomolality scale, $n_1 = 55.50843$ and $n_2 = c_{sm,2}$.

After the transform of the known formula[27] for the calculation of the apparent molar volume of the solute $V_{\phi,2}$ into the form

$$n_2V_{\phi,2} = n_1M_1^*/\rho_s + n_2M_2^*/\rho_s - n_1M_1^*/\rho_1^*, \qquad (3)$$

taking into account Eq. (2), we obtain the expression

$$V_s = n_1V_1^* + n_2V_{\phi,2}, \qquad (4)$$

where $V_1^* = M_1^*/\rho_1^*$ is the molar volume of the solvent. It follows from Eq. (4) that at $n_2 \to 0$ $V_{\phi,2} \to V_{\phi,2}^\infty \equiv \bar{V}_2^\infty$.

Substituting the $V_{\phi,2}(n_2)$ dependence by the appropriate approximating monotonic function, we can obtain the equation in which the coefficient of the linear term (a_1) is numerically equal to $\bar{V}_2^\infty(\equiv V_{\phi,2}^\infty)$. The second-power polynomial was used as such a model

$$V_s = n_1V_1^* + n_2V_{\phi,2}. \qquad (5)$$

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* Solvomolality $c_{sm,2}$ is the dimensionless parameter of the composition of a solution expressed by the correlation $c_{sm,2} = (n_2/n_1)55.50843$, where n_2 and n_1 are the amounts of the solute and solvent.[28] The normalizing factor of 55.50843 is numerically equal to the amount of the substance (mol) H_2O in 1000 g of water.

Table 1. Parameters in Eq. (1)[a]

T/K	a_0	$a_1 \cdot 10^3$	n	$\sigma_{0.95} \cdot 10^3$	r	Interval of x_2[b]
	g cm^{-3}					
			AN—H_2O			
278.15	0.797881	1.51283	10	1.37	0.9999	$4.5 \cdot 10^{-4}$—0.059
288.15	0.787206	1.52718	12	3.91	0.9997	$4.5 \cdot 10^{-4}$—0.052
298.15	0.776486	1.51835	12	4.75	0.9998	$4.5 \cdot 10^{-4}$—0.068
308.15	0.765600	1.53230	13	1.81	0.9999	$4.5 \cdot 10^{-4}$—0.038
318.15	0.754570	1.53666	13	2.22	0.9999	$4.5 \cdot 10^{-4}$—0.040
			AN—D_2O			
278.15	0.797894	2.23271	12	1.79	0.9999	$4.1 \cdot 10^{-4}$—0.057
288.15	0.787175	2.24218	12	2.72	0.9999	$4.1 \cdot 10^{-4}$—0.052
298.15	0.776442	2.23165	13	2.12	0.9999	$4.1 \cdot 10^{-4}$—0.063
308.15	0.765571	2.22981	11	2.96	0.9999	$4.1 \cdot 10^{-4}$—0.049
318.15	0.754486	2.22691	13	3.12	0.9999	$4.1 \cdot 10^{-4}$—0.058
			AN—MeOH			
278.15	0.797916[c]	0.221623	15	0.609	0.9973	0—0.020
288.15	0.787251[c]	0.218849	16	0.525	0.9983	0—0.022
298.15	0.776496[c]	0.243141	15	0.631	0.9981	0—0.025
308.15	0.765646[c]	0.251608	16	0.986	0.9964	0—0.025
318.15	0.754621[c]	0.242882	17	1.07	0.9929	0—0.021

[a] Designations: n is the number of experimental points in the concentration dependence of ρ_s on $c_{sm,2}(x_2)$, $\sigma_{0.95}$ is the root-mean-square error of the approximation (at the 95% confidence probability); r is the correlation coefficient.

[b] Molar fraction of water, $x_2 = c_{sm,2}/(55.50843 + c_{sm,2})$. The initial concentration corresponds to the residual (after purification of AN) content of water (H_2O, D_2O) or MeOH.

[c] Molar fraction of H_2O, $x_2 \approx 4.5 \cdot 10^{-4}$.

Table 2. Most reliable published data[9,33–35] on the density of acetonitrile (ρ_1*) at the temperatures under study[a]

T/K	ρ_1*/g cm^{-3}				Data of this work[f]	Average value
	I[b]	II[c]	III[d]	IV[e]		
278.15	0.797923	0.79781	—	—	0.79789	0.79787
288.15	0.787297	0.78720	0.787139	—	0.78719	0.78721
298.15	0.776552	0.77645	0.776549	0.77620	0.77646	0.77644
308.15	0.765683	0.76578	0.785846	0.76560	0.76559	0.76570
318.15	0.754703	—	—	0.75460	0.75453	0.75461

[a] The ρ_1* values were determined with an error not higher than $\pm 1 \cdot 10^{-5}$ g cm^{-3}.

[b] See Ref. 9.

[c] See Ref. 33.

[d] See Ref. 34.

[e] See Ref. 35.

[f] See Table 1.

The numerical values of the parameter $V_1 = 55.50843 V_1^*$ are known with a high accuracy. Therefore, we can write

$$V_s - V_1 = \bar{V}_2^{\infty} c_{sm,2} + a_2 c_{sm,2}^2 \qquad (6)$$

or in a more convenient linear form

$$(V_s - V_1)/c_{sm,2} = \bar{V}_2^{\infty} + a_2 c_{sm,2}. \qquad (7)$$

The use of this procedure for the calculation of $\bar{V}_2^{\infty}$ has certain advantages over the "standard" extrapolation procedure, because in the region of high dilutions the experimental $V_{\phi,2}(c_{sm,2})$ values, according to Eq. (5), lie in the narrow range of confidence intervals relative to the line intersecting the ordinate in the known, beforehand specified point.[36] This allows one to exclude the influence of the so-called effect of the "gramophone tube" caused by the dramatic increase in the $V_{\phi,2}$ values at $n_2 \to 0$.

The $\bar{E}_{p,2}^{\infty}$ values were calculated by differentiation of the dependence of $\bar{V}_2^{\infty}$ *vs.* temperature. For this purpose, the temperature dependence of $\bar{V}_2^{\infty}$ was approximated by the first-order equation

$$\bar{V}_2^{\infty} = b_0[\equiv \bar{V}_2^{\infty}(298.15\ \text{K})] + b_1(T - 298.15). \qquad (8)$$

Table 3. Volumetric characteristics of H_2O, D_2O, and MeOH in acetonitrile[a]

Solute	Parameter[b]	Values at temperature/K				
		278.15	288.15	298.15	308.15	318.15
H_2O	$\bar{V}_2^{\infty}$/cm^3 mol^{-1}	17.06	17.17	17.33	17.50	17.65
	$\bar{V}_2^{\infty}/V_2^*$	0.95	0.95	0.96	0.96	0.97
	$\bar{v}_2^{\infty}/v_{w,2}$	1.50	1.51	1.52	1.54	1.55
	$\bar{E}_{p,2}^{\infty}$/cm^3 mol^{-1} K^{-1}			0.0151±0.0006		
D_2O	$\bar{V}_2^{\infty}$/cm^3 mol^{-1}	16.96	17.05	17.18	17.34	17.47
	$\bar{V}_2^{\infty}/V_2^*$	0.94	0.94	0.95	0.95	0.96
	$\bar{v}_2^{\infty}/v_{w,2}$	1.49	1.50	1.51	1.52	1.53
	$\bar{E}_{p,2}^{\infty}$/cm^3 mol^{-1} K^{-1}			0.0132±0.0007		
$H_2O \rightarrow D_2O$	$\Delta_{tr}\bar{V}_2^{\infty}$/cm^3 mol^{-1}	−0.10	−0.12	−0.15	−0.16	−0.18
	$\Delta_{tr}V_2^{E,\infty}$/cm^3 mol^{-1}	−0.19	−0.20	−0.21	−0.22	−0.23
	$\Delta_{tr}\bar{E}_{p,2}^{\infty}$/cm^3 mol^{-1} K^{-1}			−0.0019±0.0009		
MeOH	$\bar{V}_2^{\infty}$/cm^3 mol^{-1}	39.36	39.89	40.35	40.86	41.48
	$\bar{V}_2^{\infty}/V_2^*$	0.99	0.99	0.99	0.99	0.99
	$-\bar{V}_2^{E,\infty}$/cm^3 mol^{-1}	0.44	0.38	0.40	0.39	0.29
	$\bar{v}_2^{\infty}/v_{w,2}$	1.82	1.84	1.86	1.88	1.91
	$\bar{E}_{p,2}^{\infty}$/cm^3 mol^{-1} K^{-1}			0.0530±0.0002		

[a] The $\bar{V}_2^{\infty}$($V_2^{E,\infty}$) values were determined with an error not higher than ±0.03 cm^3 mol^{-1}. Comparative data[9] on $\bar{V}_2^{\infty}$(H_2O): 17.31 (278.15 K), 17.48 (288.15 K), 17.58 (298.15 K), 17.74 (308.15 K), and 17.90 (318.15 K).

[b] The values $v_{w,2}(H_2O) = 18.9 \cdot 10^{-24}$ cm^3 molec.$^{-1}$ and $v_{w,2}(\mathrm{MeOH}) = 36.0 \cdot 10^{-24}$ cm^3 molec.$^{-1}$.[38] It is postulated that $v_{w,2}(H_2O) \approx v_{w,2}(D_2O)$ and $v_{w,2}$ is independent of T (in the indicated temperature interval).

Then, we obtain

$$[\partial\bar{V}_2^{\infty}/\partial(T - 298.15)]_p = b_1.$$

In order to find the numerical $V_{1,2}^E$ values, the following equation[37] (expressed in the scale of solvomolality concentrations) was used:

$$V_{1,2}^E = V_{1,2} - n_1V_1^*/(n_1 + n_2) - n_2V_2^*/(n_1 + n_2), \qquad (9)$$

where $V_{1,2} = [(1 - x_2)M_1^* + x_2M_2^*]/\rho_s$ is the average molar volume of the solution (the formula for the calculation of x_2 is given in the footnote[b] in Table 1).

The results of calculations of the volumetric characteristics of the solutes under study dissolved in AN are presented in Table 3 and in Figs. 1 and 2.

Results and Discussion

As already mentioned, water is dissolved in AN with a considerable endothermic effect. This suggests that the H_2O—AN interaction is weaker than the interaction of the molecules in the individual medium of each water isotopomer. In fact, according to the published data,[2,8] AN molecules form hydrogen bonds with H_2O molecules in an acetonitrile medium with an energy about −15 kJ mol^{-1}. However, the $\Delta_{sol}H_2^{\infty}$ value does not provide a complete information on the energy changes in the solvent structure induced by the solvation of water molecules.

According to the Dack concept[39] based on the use of the internal pressure of the liquid $p_{int,i}^* \approx T\alpha_{p,i}^*/\beta_{T,i}^*$ as a measure of the "volumetric" energy of universal interactions, the contribution of the energy of specific contacts ($U_{sp,i}^* = \Delta_{vap}H_i^{0,*} - RT - p_{int,i}^*V_i^*$) between the molecules in individual aqueous and acetonitrile media is ~38.9 and ~9.9 kJ mol^{-1}, respectively. For aprotic dipolar solvents similar to AN, in the framework of the model indicated, the $U_{sp,i}^*$ value characterizes the energy of

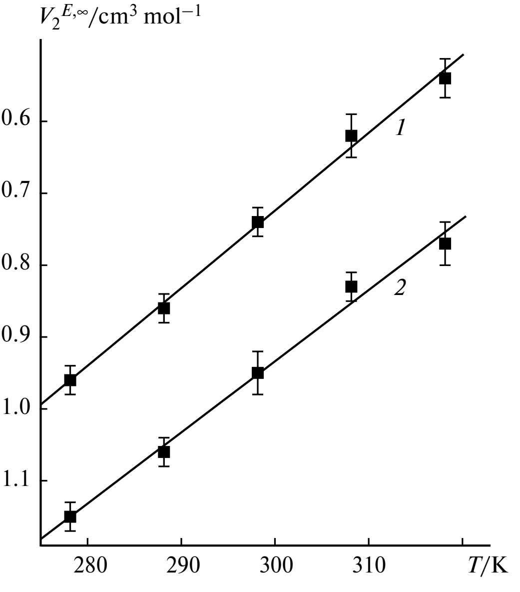

Fig. 1. Temperature dependences of the limiting excess molar volumes of H_2O (*1*) and D_2O (*2*) in acetonitrile. Confidence intervals are designated by vertical bars.

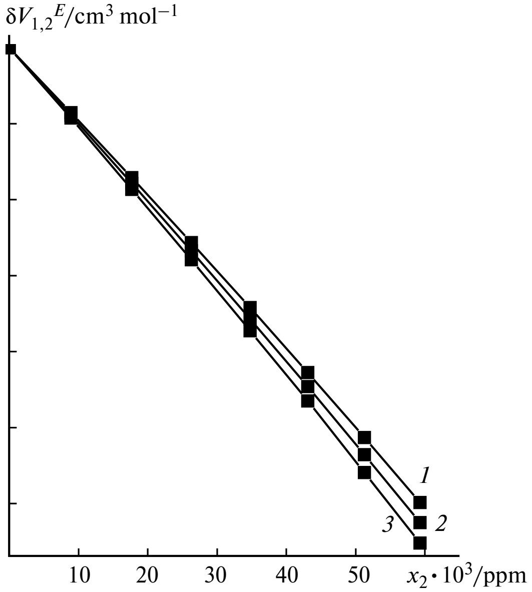

Fig. 2. Dependences of the isotope effects on the excess molar volumes of dilute acetonitrile solutions of water on its concentration (x_2) at 278.15 (*1*), 298.15 (*2*), and 318.15 K (3).

strong dipole-dipole interactions. The fact of a substantial difference between the $U_{sp,2}{}^*$ and $U_{sp,1}{}^*$ values, along with the higher electron-acceptor ability of water,[15] suggests that the molecular affinity AN—H_2O in an infinitely dilute acetonitrile solution of water is higher than the AN—AN affinity in the solvent bulk. The replacement $H_2O \rightarrow D_2O$ should increase this difference due to the enhancement of the electron-acceptor character of the molecules.[40]

Unfortunately, published data on the heats of dissolution of D_2O in AN, which could confirm or reject the above assumptions, are lacking. However, let us try to do it on the basis of analysis of the isotope effects on the limiting partial $\delta \bar{V}_2{}^\infty$ and excess $\delta V_2{}^{E,\infty}$ molar volumes and expansibilities $\delta \bar{E}_{p,2}{}^\infty$, as well as other volumetric characteristics of water in AN, namely, the $\bar{V}_2{}^\infty/V_2{}^*$ ratios of the limiting partial molecular volumes of water to their van der Waals volume $\bar{v}_2{}^\infty/v_{w,2}$ (see Table 3).

The temperature dependences of $V_2{}^{E,\infty}(H_2O)$ and $V_2{}^{E,\infty}(D_2O)$ are presented in Fig. 1. By definition,[2] the limiting excess molar volume $V_2{}^{E,\infty}$ corresponds to a change in the volume of the solute in the isobaric-isothermic process of replacement of the own environment of the H_2O and D_2O molecule by the infinitely great number of the AN molecules, *i.e.*, $V_2{}^{E,\infty} = \bar{V}_2{}^\infty - V_2{}^*$. For this reason, the isotope effect $\delta V_2{}^{E,\infty}$(AN, $H_2O \rightarrow D_2O$) differs from the $\delta \bar{V}_2\infty$(AN, $H_2O \rightarrow D_2O$) value because it contains no contribution caused by the difference in the values of the molar volumes of normal and heavy water.

It is seen from the data in Table 3 and in Fig. 1 that the partial molar volumes of both H_2O and D_2O in AN only insignificantly differ from the molar volumes of the solutes indicated. The ratio is $\bar{V}_2\infty/V_2{}^* \approx 1$, and $\bar{v}_2{}^\infty/v_{w,2} \approx v_2{}^*/v_{w,2}$. This shows that the volumes of the "free space" near the water molecules in an infinitely dilute acetonitrile solution and in an aqueous medium are comparable (especially at high temperatures).

The isotope effects of $\delta \bar{V}_2{}^\infty$ and $\delta V_2{}^{E,\infty}$ in an acetonitrile solution of water are negative and increase in the absolute value with temperature (see Table 3). The difference between these values corresponds to the change in the molar volume of water $\delta V_2{}^*$ upon the replacement $H_2O \rightarrow D_2O$.

The limiting partial molar expansibilities of H_2O and D_2O in AN exceed the molar expansibilities of the neat water isotopomers $E_{p,2}{}^*$[41] by 3.3 and 3.8 times, respectively (at 298.15 K).

The obtained volumetric characteristics of H_2O and D_2O in AN can be considered as experimental facts that additionally confirm the earlier[2,5,12,24,42,43] conclusions based on the spectroscopic results, which show that structural fragments associated by H bonds can be formed from the H_2O molecules in AN. The IR spectroscopic data[5,12,42,43] indicate that an acetonitrile solution of water contains (in addition to the MeCN...HOH complexes) hydrogen bonds formed by H_2O molecules and Me groups of AN molecules.

It follows from our data that the "water—AN" molecular aggregates with deuterium bonds are stronger than the solvate complexes formed due to H bonds, although, as a whole, the stability of both aggregates is lower than that in the structural matrices of normal and heavy water.

The compactness of the molecular packing in the (D_2O)—AN complexes with a hydrogen bond formed due to the interaction with H_2O is close to that in neat water (see Table 3) but the packing has, most likely, a different structure. Based on the data on the volumetric effect of dissolution of H_2O and D_2O (see Fig. 1) and available data,[24] we can assume that the incorporation of water molecules into the AN medium does not noticeably change the solvent structure, which is characterized by the low stability of its dimers and other associates.

The dependences of the isotope effects on the excess molar volumes of the AN—H_2O mixture on their decomposition in the region of high dilutions (relative to the water content) at different temperatures are presented in Fig. 2. It is seen that the $\delta V_{1,2}{}^E$ values, as the above considered isotope effects on the limiting volumetric characteristics of the solute (see Table 3), are small and depend weakly on temperature. This fact confirms the assumption that substantial configurational changes in the AN—H_2O system induced by the influence of dissolved water on the solvent structure are absent. Evidently, the conclusion[26] that the isotope effects on the excess volumetric and other properties of H_2O and D_2O in AN are mainly determined by the difference in energies of the hydrogen and deuterium bonds is correct.

Meanwhile, despite the analysis of the experimental data performed using even such a fine tool as isotope substitution, we failed to find unambiguous answers to all questions. One of them, perhaps most important, was formulated in the beginning of Results and Discussion. It is related to the establishment of a correlation between the energy characteristics (affinity parameters of the AN—AN and H_2O—AN interactions).

This problem can be solved in part using the approach developed by Ben-Naim,[44] according to which

$$\Delta G^{*,0} = kT\rho_1^*(\bar{V}_2^{\infty} - V_1^*) = RT(\bar{V}_2^{\infty} - V_1^*)/V_1^*. \quad (10)$$

Here k is the Boltzmann constant, and $\rho_1^* = N_A/V_1^*$ is the "number" density of particles. Based on the limiting expressions of the Kirkwood—Buff (KB) theory for molar volumes, we can interpret the $\Delta G^{*,0}$ parameter as follows. Since

$$\bar{V}_2^{\infty} = [1 - \rho_1^*(G_{11}^0 - G_{12}^0)]/\rho_1^*, \quad (11)$$

where G_{11}^0 and G_{12}^0 are the KB integrals, Eq. (10) can be transformed as follows:

$$\Delta G^{*,0} = kT\rho_1^*(G_{11}^0 - G_{12}^0) = RT(G_{11}^0 - G_{12}^0)/V_1^*. \quad (12)$$

It follows from Eqs. (10) and (12) that

$$G_{11}^0 - G_{12}^0 = \bar{V}_2^{\infty} - V_1^*. \quad (13)$$

Thus, the $\Delta G^{*,0}/kT\rho_1^*$ value can be considered as a measure of the relative affinity of molecules in the solvent—solvent (1—1) and solvent—solute (1—2) systems.

The $\bar{V}_2^{\infty} - V_1^*$ and $\Delta G^{*,0}$ values for solutions of H_2O, D_2O, and MeOH in AN are presented in Table 4. The results of studying the volumetric properties of MeOH dissolved in an acetonitrile medium are shown in Table 3. It is seen from the data in Table 4 that for all substances $\bar{V}_2^{\infty} - V_1^* < 0$ and $\Delta G^{*,0} < 0$, *i.e.*, $G_{11}^0 < G_{12}^0$. This allows us to draw the general conclusion that the water (or MeOH)—AN affinity prevails over the affinity of the solvent molecules to each other. The partial replacement of the AN—AN bond by the water (or MeOH)—AN bonds results in the condensation of the structure due to the formation of a more compact packing of molecules in the acetonitrile medium surrounding the solute. The observed increase in $\Delta G^{*,0}$ with temperature is probably related to the faster decrease in the G_{11}^0 component than the G_{12}^0 decrease due to the lower stability of molecular bonds in the solvent bulk.

Table 4. Numerical values of the parameters $(\bar{V}_2^{\infty} - V_1^*)$/cm^3 mol^{-1} (I) and $-\Delta G^{*,0}$/kJ mol^{-1} (II) for solutions of H_2O, D_2O, and MeOH in acetonitrile* at different temperatures

T/K	H_2O		D_2O		MeOH	
	I	II	I	II	I	II
278.15	34.39	1.545	34.49	1.550	12.09	0.543
288.15	34.98	1.607	35.10	1.613	12.26	0.563
298.15	35.54	1.666	35.69	1.673	12.52	0.587
308.15	36.11	1.726	36.27	1.734	12.75	0.609
318.15	36.75	1.787	36.93	1.796	12.92	0.628

* The data on V_1^* at all temperatures under study were calculated on the basis of the average ρ_1^* values presented in Table 2.

Although MeOH as a solvent is "water-like" in terms of several properties (the strong H bond, pronounced local ordering),[45] its volumetric properties in AN, as can be seen from the data in Table 4, differ significantly from analogous characteristics of water. These differences are manifested, first of all, as much lower (than those in the case of acetonitrile solutions of H_2O and D_2O) values of the AN—MeOH molecular affinity. A possible consequence of this inequality is that the limiting partial molar volumes of MeOH in acetonitrile are virtually equal to the molar volumes of the individual solute ($\bar{V}_2^{\infty}/V_2^*$), and the ratio is $\bar{\upsilon}_2^{\infty}/\upsilon_{w,2} \approx \upsilon_2^*/\upsilon_{w,2} \approx 1.86$ (at 298.15 K). The $\bar{E}_{p,2}^{\infty}$(MeOH) value differ slightly from the molar expansibility ($E_{p,2}^*$) of neat alcohol (see Table 3). In our opinion, this is associated with the fact that the MeOH molecules are easily incorporated in the AN structure forming no stable complexes with a hydrogen bond or such structures that are energetically and topologically (by the degree of their packing) similar to the chain associates in liquid MeOH.

Note that, according to Eqs. (5) and (6), the positive sign of $\bar{E}_{p,2}^{\infty}$ is determined by the inequality $(\partial V_s/\partial T)_p > (\partial V_1^*/\partial T)_p$. Thus, in the presence of dissolved water and methanol, AN gains a greater expansibility, which is probably related to the fact that the formation of new structural fragments with stronger (than in the solvent bulk) bonds weakens the AN—AN interactions and, as a consequence, loosens the solvent structure as a whole.

A similar conclusion can be obtained analyzing the temperature dependence of $\bar{V}_2^{\infty}$ on the basis of one of the known Maxwell cross-equations

$$(\partial \bar{V}_2^{\infty}/\partial T)_p = -(\partial \bar{S}_2/\partial p)_T^{\infty}. \quad (14)$$

It follows from this equation that $(\partial \bar{S}_2/\partial p)_T^{\infty} < 0$ in this case, *i.e.*, the system becomes more prone to the disintegrating effect of the pressure due to the weakening of the overall bonding.

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