COMPETITION BETWEEN H₂O AND CH₃OH MOLECULES IN THE FORMATION OF THE SIMPLEST STABLE PROTON DISOLVATES AND THEIR SOLVATION IN AQUEOUS METHANOL SOLUTIONS OF KOH AND CH₃OK

E. G. Tarakanova[1], G. V. Yukhnevich[1],
I. S. Kislina[2], and V. D. Maiorov[2]

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IR spectroscopic and quantum chemical methods are used to study the competition between water and methanol molecules in the formation of the simplest stable proton disolvates and their subsequent solvation in the case of solutions of KOH in CH₃OH and CH₃OK in H₂O with similar stoichiometries (~1:3-3.5). The complexes found in these solutions are analysed to determine their composition and structure: they are found to be heteroions $(CH_3O\cdots H\cdots OH)^-$ solvated by two similar solvent molecules. In both cases, there are virtually no complexes of the second possible type $(CH_3OH\cdot(CH_3O\cdots H\cdots OCH_3)^-\cdot H_2O$ or $CH_3OH\cdot(HO\cdots H\cdots OH)^-\cdot H_2O)$, which appears to be due to the stoichiometric compositions of the solutions. It is shown that a DFT calculation (B3LYP/6-31++G(d,p)) of linear complexes with strong (~15-30 kcal/mol) H bonds reproduces, with good accuracy, the IR spectra of the solutions, which consist mainly of these complexes.

INTRODUCTION

One of the relevant problems of acid–base catalysis is to understand the mechanism underlying the catalytic action of solutions of strong bases. Solving this problem involves the study of the composition, structure, and formation conditions of the simplest stable OH⁻ ion solvates [1-3]. It is now known that the dissociation of hydroxides and alkoxides in aqueous, alcoholic, and water-alcohol solutions leads to the formation of negatively charged proton disolvates with a strong quasi-symmetric H bond $((HO\cdots H\cdots OH)^-, (RO\cdots H\cdots OH)^-,$ or $(RO\cdots H\cdots OR)^-)$, which experience further solvation [3-7]. A characteristic feature of the IR spectra of these ions is intense continuous absorption (CA) in the frequency range from 700 cm⁻¹ to 3500 cm⁻¹ [6-9].

The catalytic activity of strong base solutions depends on the equilibrium composition of the ions present in the solutions and the concentration ratio of the solvent components [10]. It should be noted that there is a competition between

[1]Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia; egtar@igic.ras.ru. [2]Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 58, No. 1, pp. 74-82, January-February, 2017. Original article submitted March 29, 2016.

solvent molecules not only in the stage of formation and solvation of proton disolvates but also in the stage of formation of the original ion, which is part of the proton disolvate composition [11-13]

$$OH^- + ROH \leftrightarrow H_2O + RO^-. \tag{1}$$

A shift of the state of equilibrium (1) changes the concentration ratio of the hydroalcoholic solvent components.

A good choice for practical use as catalytic media is water-alcohol hydroxide solutions because of the much higher solubility of organic substrates in these solutions than in aqueous alkaline ones and the higher solubility of alkoxides than in alcoholic solutions [5]. To predict the catalytic activity of water-alcohol hydroxide solutions, one needs to know the composition of the corresponding simplest stable proton disolvates and their solvation shells.

The aim of this work was the IR spectroscopic and quantum chemical study of the competition between water and methanol molecules in the formation of simplest stable proton disolvates and their subsequent solvation in aqueous methanol solutions of strong bases. The objects of research were solutions of CH_3OK in CH_3OH, KOH in CH_3OH, and CH_3OK in H_2O. It was assumed that the combination of the two methods would allow us to identify the composition and structure of the proton disolvates forming in these solutions and to determine for each disolvate the nature of its solvation by solvent molecules.

EXPERIMENTAL

The solutions were prepared from chemically pure KOH, CH_3OK, and CH_3OH and double-distilled water by the weight method. The molar concentrations of the components were calculated by measuring the density of the solutions.

The IR spectra were recorded at a temperature of 30 °C by the multiple frustrated total internal reflection (MFTIR) method [14]. The MFTIR attachment had Ge prisms to achieve an angle of incidence of 30° and a number of reflections of 8 or 10 (depending on the thickness of the crystal) when both of the cavities at the Ge crystal were filled with the solution. The effective thickness of the absorbing layer at a frequency of 2000 cm^{-1} was 3.37 μm or 4.21 μm, respectively. The spectra were recorded in the frequency range from 700 cm^{-1} to 4000 cm^{-1}.

RESULTS AND DISCUSSION

Fig. 1 shows the MFTIR IR spectra of the CH_3OK and KOH solutions in methanol and water. The stoichiometric compositions of these solutions are given in Table 1. Note that the compositions of solutions **2** and **3** were such that the most part of solvent molecules took part either in the formation or solvation of proton disolvates, which made it easier to compare the calculated and experimental spectra (since the latter had no bands associated with free solvent molecules). All the spectra have CA in a broad frequency range; several bands of various intensity manifest themselves against this CA background. The available literature data [4-6] enable a comparison of molar CA coefficients (ε_{CA}) in the IR spectra of methanol and aqueous methanol solutions of KOH and CH_3OK. Fig. 2 shows the dependences of the optical densities of CA at 2000 cm^{-1} on the
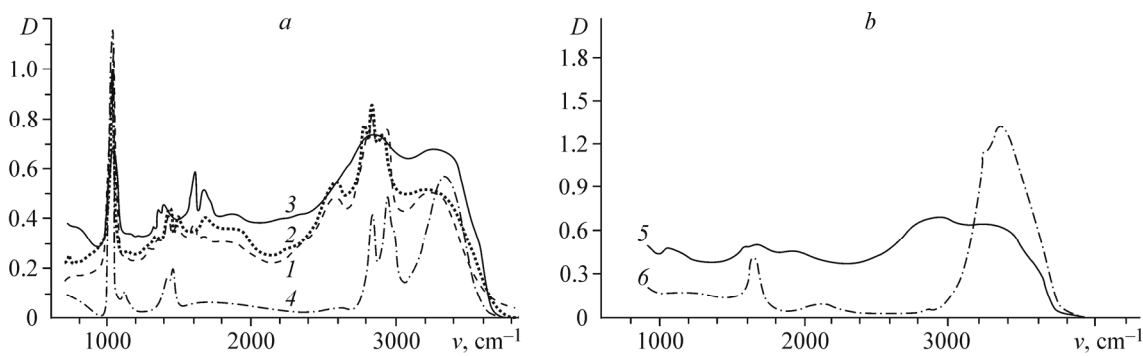

Fig. 1. MFTIR IR spectra of the solutions: CH_3OK in CH_3OH (*1*), KOH in CH_3OH (*2*), CH_3OK in H_2O (*3*), CH_3OH (*4*), KOH in H_2O (*5*), and H_2O (*6*).

TABLE 1. Stoichiometric Compositions of the Solutions

Solution composition	$[KOH]_0$, mol/l	$[CH_3OK]_0$, mol/l	$[CH_3OH]_0$, mol/l	$[H_2O]_0$, mol/l
Solution **1** CH_3OK in CH_3OH	0	5.23	20.86	0
Solution **2** KOH in CH_3OH	6.86	0	21.79	0
Solution **3** CH_3OK in H_2O	0	9.6	0	35.68
Solution **4*** KOH in H_2O	14.13	0	0	40.70

* The data are from [6].
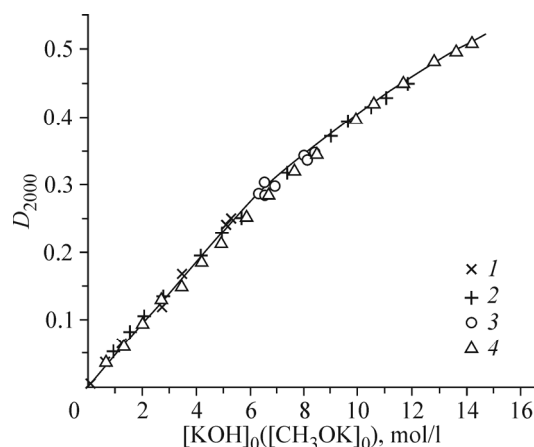
Fig. 2. Dependences of the optical density D_{2000} on the concentrations of CH_3OK (*1*) and KOH (*2*)-(*4*) in solutions: CH_3OH (*1*), 10 mol.% CH_3OH – 90 mol.% H_2O (*2*), from 20 mol.% to 85 mol.% CH_3OH – from 80 mol.% to 15 mol.% H_2O (*3*), and H_2O (*4*).

base concentrations in these solutions. The growth of D_{2000} slows down in concentrated KOH solutions since the degree of solvation of the proton solvates in these solutions decreases from two to one.

It is evident from Fig. 2 that, regardless of the composition of the central ion – $(HO\cdots H\cdots OH)^-$, $(CH_3O\cdots H\cdots OH)^-$, or $(CH_3O\cdots H\cdots OCH_3)^-$ –and its solvation by water or methanol molecules, the experimental data fit into a single curve. This means that the molar CA coefficients of the said particles at 2000 cm^{-1} are the same. A similar pattern for ε_{CA} is also observed at other CA frequencies. Thus, the values of ε_{CA} cannot be used to trace the competition between H_2O and CH_3OH molecules in the formation of ions with strong quasi-symmetric H bonds and their solvation in aqueous methanol solutions of KOH and CH_3OK. Therefore, the recorded IR spectra can only be interpreted using data on the vibration frequencies of solvated ions that can form in the solutions as a result of the competition between water and methanol molecules.

A study of solvation of $(HO\cdots H\cdots OH)^-$, $(CH_3O\cdots H\cdots OH)^-$, and $(CH_3O\cdots H\cdots OCH_3)^-$ ions in solutions showed that solvation by two solvent molecules is most beneficial in terms of energy [5, 6]. If the solvent concentration is insufficient for this solvation, the solution contains a mixture of ion di- and monosolvates. The stoichiometry of solutions **1**-**3** (Table 1) suggests the predominant formation of proton disolvates with strong quasi-symmetric H bonds, which are solvated by two molecules*. Therefore, to assign the absorption bands in the spectra of these solutions to the experiment, we compared the

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* In what follows, proton disolvates are called, as a rule, as $(CH_3O\cdots H\cdots OCH_3)^-$, $(CH_3O\cdots H\cdots OH)^-$, and $(HO\cdots H\cdots OH)^-$ ions and the main complexes studied in this work are called as $(CH_3O\cdots H\cdots OCH_3)^-$, $(CH_3O\cdots H\cdots OH)^-$, and $(HO\cdots H\cdots OH)^-$ ion disolvates.

calculated vibrational frequencies of $(CH_3O\cdots H\cdots OCH_3)^-$, $(CH_3O\cdots H\cdots OH)^-$, and $(HO\cdots H\cdots OH)^-$ ions in free and double-solvated (through the unshared electron pairs of oxygen atoms in the $O_1\cdots H\cdots O_2$ bridge) states.

The ion disolvate characteristics necessary to accomplish the study objective were calculated by the DFT method (B3LYP/6-31++G(d,p)) in the GAUSSIAN 09 software [15]. In so doing, we considered all the possible solvation options for each of the ions[*] – by two water molecules, by two methanol molecules, and by H_2O and CH_3OH molecules (there are two ways in which they can be arranged in the case of the $(CH_3O\cdots H\cdots OH)^-$ heteroion). The main[**] energy and structural parameters of all the systems are given in Table 2, and the derived data on the proton affinity (PA) of the particles under consideration are given in Table 3. The calculated PA values were compared with those known from the experiment to show that the chosen calculation method allows a good reproduction of the absolute (average error of 2.8%) and relative (average error of 0.9%) PA values of H_2O and CH_3OH molecules and their anions (Table 3). Therefore, it is appropriate to apply this method in the study of the competition between water and methanol molecules in solvation processes.

TABLE 2. Energies of Formation of Proton Disolvates (ΔE, kcal/mol) and their Solvation by Two Molecules (ΔE^{solv}, kcal/mol). Parameters of Hydrogen Bridges: Bond Lengths ($R_{O_1\cdots H}$, $r_{H\cdots O_2}$, Å), Angles γ (deg.), and the Degree of Asymmetry ($\rho = R_{O_1\cdots H} / r_{H\cdots O_2}$)

System*	ΔE and (ΔE^{solv})	$R_{O_1\cdots H}$	$r_{H\cdots O_2}$	γ	$R+r$	$\rho = R/r$
$(CH_3O\cdots H\cdots OH)^-$	25.9**, 33.4***	1.424	1.078	176	2.502	1.321
$CH_3OH\cdot(CH_3O\cdots H\cdots OH)^-\cdot H_2O$	(38.0)	1.395	1.083	178	2.478	1.288
$CH_3OH\cdot(CH_3O\cdots H\cdots OH)^-\cdot CH_3OH$	(37.1)	1.365	1.098	178	2.463	1.243
$H_2O\cdot(CH_3O\cdots H\cdots OH)^-\cdot H_2O$	(37.3)	1.340	1.114	179	2.454	1.203
$CH_3OH\cdot(HO\cdots H\cdots OCH_3)^-\cdot H_2O$	(37.2)	1.330	1.117	180	2.447	1.191
$(CH_3O\cdots H\cdots OCH_3)^-$	27.4	1.306	1.133	177	2.439	1.153
$CH_3OH\cdot(CH_3O\cdots H\cdots OCH_3)^-\cdot H_2O$	(59.0)	1.372	1.090	179	2.462	1.259
$H_2O\cdot(CH_3O\cdots H\cdots OCH_3)^-\cdot H_2O$	(58.6)	1.348	1.103	179	2.451	1.222
$CH_3OH\cdot(CH_3O\cdots H\cdots OCH_3)^-\cdot CH_3OH$	(58.7)	1.329	1.112	178	2.441	1.195
$(HO\cdots H\cdots OH)^-$	30.2	1.318	1.147	178	2.465	1.149
$CH_3OH\cdot(HO\cdots H\cdots OH)^-\cdot H_2O$	(40.1)	1.340	1.117	179	2.457	1.200
$CH_3OH\cdot(HO\cdots H\cdots OH)^-\cdot CH_3OH$	(40.2)	1.296	1.146	179	2.442	1.131
$H_2O\cdot(HO\cdots H\cdots OH)^-\cdot H_2O$	(39.7)	1.283	1.156	179	2.439	1.110

* The notation for the "original" ion first gives a long ($R_{O_1\cdots H}$) and then a short ($r_{H\cdots O_2}$) bond.
** The energy of formation of $(CH_3O\cdots H\cdots OH)^-$ from an H_2O molecule and a CH_3O^- anion.
*** The energy of formation of $(CH_3O\cdots H\cdots OH)^-$ from a CH_3OH molecule and an OH^- anion.

TABLE 3. Proton Affinity (PA, kcal/mol) of H_2O and CH_3OH Molecules and their Anions

H_2O	CH_3OH	PA_{CH_3OH}/ PA_{H_2O}	OH^-	CH_3O^-	$PA_{CH_3O^-} / PA_{OH^-}$	Source
171.7	187.1	1.090	395.3	387.8	0.981	This calculation
164	182	1.110	391	379	0.969	[16]
165.0	180.1	1.092	–	–	–	[17]
166.5	182.0	1.093	–	–	–	[18]

[*] A part of the data for the $H_3O_2^-$ ion was obtained previously from [6].

[**] Here and below, we consider only those results of the calculation that are necessary for solving the posed problem.

It is evident from the data in Table 2 that the energy of attachment of any two molecules to $(HO\cdots H\cdots OH)^-$, $(CH_3O\cdots H\cdots OCH_3)^-$, and $(CH_3O\cdots H\cdots OH)^-$ ions is virtually independent of their nature (the values of ΔE^{solv} for different molecule pairs vary in the range 1-2.5%) and depends very little on the nature of the ion (the difference in the values of ΔE^{solv} for different ions is <10%). The closeness of the strengths of the "lateral" hydrogen bridges in different ion disolvates (the variation range of their bond lengths are $r_{O_1\cdots H_1} < 4.3\%$ and $r_{O_2\cdots H_2} < 4.6\%$) suggests the closeness of the proton donating abilities of water and methanol. This conclusion is consistent with the results of experimental and calculation studies [19-22], from which it follows that the relative difference of the proton-donating abilities of the molecules is less than the difference in their proton accepting properties (as is evident from Table 3, this difference is ~9%). In this case, H_2O and CH_3OH molecules have approximately the same chance to find themselves in the solvate shell of an ion, and the composition of the shell depends on the ratio between the equilibrium concentrations of those molecules of the two solvents that are not part of proton disolvates.

It should be noted that the lengths of the $O_1\cdots H\cdots O_2$ bridges in the ions (2.47±0.03 Å) and their angles γ (178±2°) are weakly dependent on the ion disolvate composition whereas the degree of asymmetry of the bridges ($\rho = R_{O_1\cdots H}/r_{H\cdots O_2}$) is strongly dependent on this composition (Table 2). The ratios between the lengths of H bonds in the homoions $(HO\cdots H\cdots OH)^-$ ($\rho = 1.149$) and $(CH_3O\cdots H\cdots OCH_3)^-$ ($\rho = 1.153$) are virtually the same. The most asymmetric bridge ($\rho = 1.321$) is the longest one $O_1\cdots H\cdots O_2$ ($R_{O_1O_2} = 2.502$ Å), which belongs to the heteroion, and the least asymmetric bridge ($\rho = 1.110$) is a short bridge of the $(HO\cdots H\cdots OH)^-$ ion dihydrate ($R_{O_1O_2} = 2.439$ Å). The dependence between the degree of asymmetry and the length of $O_1\cdots H\cdots O_2$ bridges in $(CH_3O\cdots H\cdots OCH_3)^-$, $(CH_3O\cdots H\cdots OH)^-$, and $(HO\cdots H\cdots OH)^-$ ion disolvates is exponential; however, in its initial interval (at $\rho < 1.17$), it is close to a linear one (Fig. 3a).

According to our calculations, the strongest bands in the IR spectrum of each complex correspond to antisymmetric stretching vibrations of the H bonds of its three hydrogen bridges[*]. The vibrations of the $O_1\cdots H\cdots O_2$ fragment, ν_{OHO}^{as} (Table 4), are, as a rule, the most intense, and the vibrations of the bridges formed by solvent molecules with O_1 ($\nu_{OHO}^{as\,R}$) and O_2 ($\nu_{OHO}^{as\,r}$) atoms are less intense (by ~20% and ~50%, respectively). Some of the ion disolvates have several vibrations, during which the central proton shifts along the H bond. All these vibrations are very likely to be visible in the absorption spectrum. With increasing proton shift from the center, the ν_{OHO}^{as} and $\nu_{OHO}^{as\,r}$ frequencies increase and $\nu_{OHO}^{as\,R}$ decreases. It also
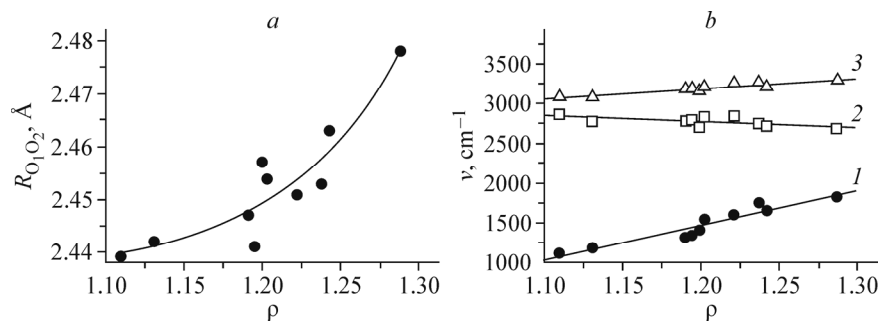
Fig. 3. Dependence of the length of the $O_1\cdots H\cdots O_2$ fragments in $(HO\cdots H\cdots OH)^-$, $(CH_3O\cdots H\cdots OCH_3)^-$, and $(CH_3O\cdots H\cdots OH)^-$ ion disolvates on the degree of its asymmetry (*a*); the dependence of the frequencies of the antisymmetric stretching vibrations associated with the ν_{OHO}^{as} (*1*), $\nu_{OHO}^{as\,R}$ (*2*), and $\nu_{OHO}^{as\,r}$ (*3*) hydrogen bridges on the degree of their asymmetry (*b*).

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[*] In what follows, we write, for brevity, "a vibration of the ν_{OHO}^{as} bridge (or fragment)" instead of "an antisymmetric stretching vibration of the H bonds of the ν_{OHO}^{as} hydrogen bridge." The ν_{OHO}^{as} vibrations of lateral bridges are, in fact, stretching vibrations of the H bonding OH groups of solvent molecules.

TABLE 4. Measured and Calculated Vibration Frequencies (ν, cm^{-1}) of the Complexes CH$_3$OH·(CH$_3$O···H···OCH$_3$)$^-$·CH$_3$OH, CH$_3$OH·(CH$_3$O···H···OH)$^-$·CH$_3$OH and H$_2$O·(CH$_3$O···H···OH)$^-$·H$_2$O, which form in Solutions **1**, **2**, and **3**, Respectively

Solution of CH$_3$OK in CH$_3$OH	(CH$_3$O···H···OCH$_3$)$^-$·2CH$_3$OH	Solution of KOH in CH$_3$OH	(CH$_3$O···H···OH)$^-$·2CH$_3$OH	Solution of CH$_3$OK in H$_2$O	(CH$_3$O···H···OH)$^-$·2H$_2$O	Assignment of vibrations*
1027	1066	1027	1095	1025	1093	ν_{CO} ($\gamma^{\perp R}$; ν_{OHO}^{as})**
1120	1116	1125	1126	~1150	1181	α_{OCH} ($\gamma^{\perp R}$)
1435	1346	1425	1442	1340	1345	α_{CH3}^{s} (ν_{OHO}^{as})
1470	1471	1480	1471	1380	1392	α_{CH3}^{s} ($\gamma^{\perp}$)
1595	1579	1680	1654	1592	1539	ν_{OHO}^{as} (α_{CH3}^{s})
1655	1622	–	1700	1650	1670	$\gamma^{\perp}$ (α_{HOH})
~2575	2789	~2580	2715	~2810****	2930	$\nu_{OHO}^{as\,R}$
~2770***	2871–3046 12 vibrations	2770***	2867–3017 9 vibrations	Not visible	2836–2898 3 vibrations	Stretching vibrations of CH$_3$ groups
2825***		2823***		Not visible		
2925***		~2890***		Not visible		
~3230	3188	~3200	3211	~3250	3199	$\nu_{OHO}^{as\,r}$

* The notation used to designate vibration modes: ν – stretching vibrations, α – deformation vibrations, $\gamma^{\perp}$ – vibrations of a bridging proton in the direction perpendicular to the bridge; ^{s} and ^{as} – symmetric and antisymmetric vibrations; and ^{R} (and ^{r}) – the designation of the natural coordinates located on the same side of the central proton as the $R_{O_1\cdots H}$ ($r_{H\cdots O_2}$) bond.

** The notation in parentheses is the natural coordinates whose changes also make a substantial contribution to the vibration

*** The frequencies of the maxima of the total band contours, which were not considered when calculating the values of δ and σ.

**** The frequency of the maximum associated with the total contour of the $\nu_{OHO}^{as\,R}$ band and the three bands of the stretching vibrations of CH$_3$ groups.

follows of the solution. The frequencies of the considered vibrations of (CH$_3$O···H···OCH$_3$)$^-$, (CH$_3$O···H···OH)$^-$, and (HO···H···OH)$^-$ ion disolvates are almost linearly dependent on the degree of asymmetry of their hydrogen bridges (Fig. 3b). from Fig. 3b that the absorption bands of the O$_1$···H···O$_2$ fragment and the bridges connecting it with solvent molecules lie in the intervals that do not intersect with one another: ~1050-1830 cm^{-1}, ~2680-2930 cm^{-1} ($\nu_{OHO}^{as\,R}$), and ~3100-3300 cm^{-1} ($\nu_{OHO}^{as\,r}$).

Now let us analyze the results of the experiment. It should be noted that the IR spectra of solutions **1** and **2** differ much less from each other than from the spectrum of solution **3** (Fig. 1). Moreover, the most substantial and the most visible differences between the three spectral curves are in the range 1330-1800 cm^{-1}. Let us begin our analysis with solution **1**. All (CH$_3$O···H···OCH$_3$)$^-$ ions in this solution are double solvated. This conclusion follows from the dependence shown in Fig. 2: all the data points for CH$_3$OK solutions in methanol lie in the linear interval of the curve.

The calculated frequencies of vibrations of the CH$_3$OH·(CH$_3$O···H···OCH$_3$)$^-$·CH$_3$OH complex were compared with those of the absorption maxima of solution **1** to show that they are in a quite good agreement. This consistency allowed us to assign the most intense band of the experimental spectrum (Table 4) and estimate the error associated with the description of the experiment by the calculation. For the estimate to be most rigorous, we used two independent parameters: the average relative deviation of the calculated frequencies from the measured ones (δ, %) and the mutual arrangement of bands in the

spectrum (σ, %). The latter parameter was estimated by taking the length of the frequency interval Δ that contains all the vibration bands being analyzed at 100%, expressing the distances $(\nu_j-\nu_i)$ between all the neighboring band pairs as percentages, and calculating the average deviation of the calculated values of $(\nu_j-\nu_i)/\Delta$ from the experimental ones. The resulting values of δ (2.88%) and σ (5.01%) reflect the accuracy with which the calculation of the vibration frequencies of an isolated H bonded complex reproduces the spectrum of a solution consisting of these complexes.

Based on the stoichiometry of solution **2**, it is most likely characterized by the formation of the complexes $CH_3OH\cdot(CH_3O\cdots H\cdots OH)^-\cdot CH_3OH$ and $CH_3OH\cdot(CH_3O\cdots H\cdots OCH_3)^-\cdot H_2O$. This solution may contain predominantly one of these complexes or their mixture. Based on the changes in the CA coefficient (Fig. 2), we estimated the percentage of ion disolvates in solution **2**. The estimate showed that ion disolvates account for no less than 90% of all the ions in the solution (the other ions form an H bond with one of the solvent molecules). Therefore, it is appropriate to compare the IR spectrum of solution **2** with the calculated spectra of the complexes $CH_3OH\cdot\cdot(CH_3O\cdots H\cdots OH)^-\cdot CH_3OH$ and $CH_3OH\cdot(CH_3O\cdots H\cdots OCH_3)^-\cdot H_2O$.

As a result of this comparison, we found that only the frequencies of the $CH_3OH\cdot(CH_3O\cdots H\cdots OH)^-\cdot CH_3OH$ complex were consistent with the experiment (Table 4): δ = 2.23% and σ = 3.28%. The measured spectrum had no explicit signs of the presence of $CH_3OH\cdot(CH_3O\cdots H\cdots OCH_3)^-\cdot H_2O$ complexes in the solution. Otherwise, it would have necessarily had a band located ~100 cm^{-1} above the band at 1680 cm^{-1}. Similarly, we showed that solution **2** did not contain any other ion disolvates in quantities detectable by IR spectroscopy.

There is a similar situation with solution **3**, whose stoichiometric composition shows that it may contain high concentrations of $H_2O\cdot(CH_3O\cdots H\cdots OH)^-\cdot H_2O$ and $CH_3OH\cdot(HO\cdots H\cdots OH)^-\cdot H_2O$ complexes or their mixture. The percentage of the ion disolvates, which was estimated from the change in the value of ε_{2000}, is in this case ~80%. A comparison of the vibrational spectra of the two complexes with the experiment showed that the heteroion dehydrate $H_2O\cdot(CH_3O\cdots H\cdots OH)^-\cdot H_2O$ is virtually the only complex formed in solution **3**. Its calculated spectrum is well consistent with the measured one (Table 4): δ = 2.62% and σ = 3.35%. Vibrational spectroscopy detected neither the $CH_3OH\cdot(HO\cdots H\cdots OH)^-\cdot H_2O$ complex nor any other ion disolvates in solution **3**.

Now we shall try to understand why it is heteroion disolvates that form in the solutions under study. It follows from the values of the formation and solvation energies of $(CH_3O\cdots H\cdots OH)^-$, $(CH_3O\cdots H\cdots OCH_3)^-$, and $(HO\cdots H\cdots OH)^-$ ions (Table 2) that the $CH_3OH\cdot\cdot(CH_3O\cdots H\cdots OH)^-\cdot CH_3OH$ complex ($\Delta E + \Delta E^{solv}$ = 70.5 kcal/mol), which dominates in solution **2**, is less beneficial in terms of energy than $CH_3OH\cdot(CH_3O\cdots H\cdots OCH_3)^-\cdot H_2O$ ($\Delta E + \Delta E^{solv}$ = 86.4 kcal/mol). The same situation is observed in solution **3**. The $H_2O\cdot(CH_3O\cdots H\cdots OH)^-\cdot H_2O$ complex ($\Delta E + \Delta E^{solv}$ = 63.2 kcal/mol) that is present in this solution is less stable than $CH_3OH\cdot(HO\cdots H\cdots OH)^-\cdot H_2O$ ($\Delta E + \Delta E^{solv}$ = 70.3 kcal/mol). It means that the decisive role in the formation of ion disolvates in solutions of strong bases is played by some unknown factor rather than the total energy $\Delta E + \Delta E^{solv}$.

Let us assume that this factor is ΔE, a characteristic of the proton disolvate. In solution **2**, the energy of formation of a heteroion from a CH_3OH molecule and OH^- ion (ΔE = 33.4 kcal/mol) largely exceeds the energy of formation of an $(CH_3O\cdots H\cdots OCH_3)^-$ ion (ΔE = 27.4 kcal/mol), which can only appear in this solution if equilibrium (1) shifts rightward. In solution **3**, in contrast, the energy of formation of a heteroion from an H_2O molecule and CH_3O^- ion (ΔE = 25.9 kcal/mol) is less than the energy of formation of an $(HO\cdots H\cdots OH)^-$ ion (ΔE = 30.2 kcal/mol). Therefore, ΔE is not a decisive factor. However, a necessary condition for the appearance of a homoion in this solution as well is a shift of equilibrium (1) in the opposite direction (in this case, leftward).

Thus, a virtual absence or a low (up to ~10-15%) content of the second possible type of complexes in solutions **2** and **3** ($CH_3OH\cdot(CH_3O\cdots H\cdots OCH_3)^-\cdot H_2O$ in solution **2** and $CH_3OH\cdot(HO\cdots H\cdots OH)^-\cdot H_2O$ in solution **3**) can be formally explained by a substantial shift of equilibrium (1) in these solutions (leftward in solution **2** and rightward in solution **3**). In

both cases, solvated $(CH_3O\cdots H\cdots OH)^-$ ions (we denote them as $(CH_3O\cdots H\cdots OH)^-_{solv}$) are intermediate complexes formed in the course of reaction (1)

$$OH^- + CH_3OH \leftrightarrow (CH_3O\cdots H\cdots OH)^-_{solv} \leftrightarrow H_2O + CH_3O^-.$$
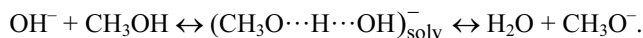
In both cases, i.e., when KOH is dissolved in methanol and CH_3OK is dissolved in water, $(CH_3O\cdots H\cdots OH)^-$ ions are the first to form. They can be solvated (as follows from the compositions of solutions **2** and **3**) only by similar solvent molecules: methanol and water, respectively. The $(CH_3O\cdots H\cdots OH)^-_{solv}$ complexes[*] have the strongest H bonds in the solution[**]. In ~80-90% of these complexes, the heteroion is double solvated, i.e., is in a state that is most beneficial for it in terms of energy. Moreover, the both solutions have a low (~10-20%) concentration of solvent molecules that are not part of the solvate shell of the $(CH_3O\cdots H\cdots OH)^-$ ion. The influence of these molecules through cooperative or other mechanisms might have led to a change in the composition of the central ion and the appearance of $(CH_3O\cdots H\cdots OCH_3)^-_{solv}$ (for KOH dissolved in methanol) or $(HO\cdots H\cdots OH)^-_{solv}$ complexes (for CH_3OK dissolved in water).

The composition of the central ion is most likely to change when $(CH_3O\cdots H\cdots OH)^-$ ions are solvated by one water molecule and one methanol molecule, which is the case of the $CH_3OH\cdot(HO\cdots H\cdots OCH_3)^-\cdot H_2O$ complex (Table 2). This type of solvation, which leads to a transfer of the central proton form the OH^- ion to the CH_3O^- ion and weakening of the both bonds in the bridge, will be observed in solutions of KOH and CH_3OK in water–methanol mixtures. Depending on the concentration ratio of the solvent components, these solutions will simultaneously contain the heterodisolvates and one of the homodisolvates in different proportions (as is the case in aqueous methanol solutions of acids [23, 24]). The fact that $(CH_3O\cdots H\cdots OH)^-_{solv}$ ions were almost the only ones to be present in the KOH solutions in methanol and CH_3OK solutions in water can be due to the stoichiometric compositions of the solutions, which provide conditions for the formation of $(CH_3O\cdots H\cdots OH)^-$ heteroions and their solvation by similar solvent molecules.

CONCLUSIONS

IR spectroscopic and quantum chemical methods were used to study the competition between water and methanol molecules in the formation of the simplest stable proton disolvates and their subsequent solvation in solutions of KOH in CH_3OH and CH_3OK in H_2O with similar stoichiometries (~1:3-3.5).

The composition and structure of the complexes present in these solutions were determined: they are $(CH_3O\cdots H\cdots OH)^-$ heteroions solvated by two similar solvent molecules. We suggested that the virtual absence of the second possible type of complexes $(CH_3OH\cdot(CH_3O\cdots H\cdots OCH_3)^-\cdot H_2O$ or $CH_3OH\cdot(HO\cdots H\cdots OH)^-\cdot H_2O)$ in both cases is due to the stoichiometric compositions of the solutions.

It is revealed that the position of the proton in the bridges of $(CH_3O\cdots H\cdots OCH_3)^-$, $(CH_3O\cdots H\cdots OH)^-$, and $(HO\cdots H\cdots OH)^-$ ions and the frequencies of stretching vibrations of these bridges are noticeably dependent on the nature of solvation of the ion by solvent molecules. The intensive absorption bands of the three hydrogen bridges of each of the complex lie in frequency intervals that do not overlap one another.

It is shown that a DFT (B3LYP/6-31++G(d,p)) calculation of the complexes with a linear structure and strong (~15-30 kcal/mol) H bonds reproduces, with a good accuracy, the experimental IR spectra of the solutions, which consist mainly of these complexes.

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[*] The parameters of their $O_1\cdots H\cdots O_2$ bridges are close to those of the optimal configuration of the heteroion; i.e., the proton is located closer to the oxygen atom of the hydroxyl ion than to that of the methylate ion.

[**] The $R_{O_1\cdots H}$, $r_{O_1\cdots H_1}$, and $r_{O_2\cdots H_2}$ distances, expressed as percentages of $r_{H\cdots O_2}$, are 124%, 141%, and 153% in the $CH_3OH\cdot(CH_3O\cdots H\cdots OH)^-\cdot CH_3OH$ complex and 120%, 144%, and 152% in the $H_2O\cdot(CH_3O\cdots H\cdots OH)^-\cdot H_2O$ complex.

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