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KINETICS AND MECHANISM OF CHEMICAL REACTIONS. CATALYSIS

$H_3O_2^-$ Ions with a Strong Quasi-Symmetrical H-Bond and Their Hydration in Aqueous Solutions of NaOH and KOH

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Abstract—Ion-molecular interactions in aqueous solutions of NaOH (0–47.8%) and KOH (0–51.95%) are studied by multiple frustrated total internal reflection IR spectroscopy. Interpretation of the spectra and analysis of the spectral data are performed based on the results of DFT calculations (B3LYP/6-31++G(*d*, *p*)) of the characteristics of the free and double hydrated $H_3O_2^-$ ion. It is established that the changes in the IR spectra of NaOH and KOH aqueous solutions caused by increasing alkali concentration are due to the formation of $H_3O_2^-$ ions with a strong quasi-symmetrical hydrogen bond and their subsequent hydration by one or two water molecules. The influence of the cation nature on the degree of hydration of $H_3O_2^-$ ions is demonstrated. The equilibrium concentrations of monohydrate ($H_3O_2^- \cdot H_2O$) and dihydrate ($H_3O_2^- \cdot 2H_2O$) are calculated and their IR continuous absorption spectra are isolated.

Keywords: IR spectra, hydrogen bond, proton disolvates, solvation, NaOH, KOH, aqueous solutions
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Recent times have seen a renewed interest in studying the state of the hydroxyl ion in aqueous alkaline solutions with the aim to clarify the mechanism of electric conductivity, ion transport in biological systems, catalytic transformations of organic compounds in solutions of bases [1–8]. To solve these problems it is necessary to know the composition and structure of the simplest stable species produced in such solutions, as well as the characteristics of their subsequent hydration.

It can now be regarded as established that the dissociation of acids in an aqueous medium produces $H_5O_2^+$ ions with a strong symmetrical hydrogen bond (simplest stable proton hydrates), which are subjected to further hydration [9–15]. Along with this, various methods have shown the presence of negative ions of similar structure in the solid and liquid phase, more specifically, homoconjugation anions AHA^- with a quasi-symmetric bridge $(O...H...O)^-$ [16–19]. However, the possibility of the formation of $H_3O_2^-$ species of similar structure, $(HO...H...OH)^-$, in aqueous alkaline solutions is still not recognized by all the authors. The main arguments against the formation of such ions in solutions are the results of a series of quantum-chemical calculations of the structure of $OH^- \cdot nH_2O$ clusters in the gas phase and in the polarizable cavity approximation, according to which the most stable is the $OH^- \cdot 3H_2O$ pyramidal structure, corresponding to the global minimum [2, 20–23]. The validity of this model for the liquid phase is justified by the presence of an intense line at 3600 cm^{-1} in Raman spectra (RS) of aqueous alkaline solutions, assigned to the vibration of the hydroxide ion, which is obviously not enough. The proposed model does not account for the specific features of the IR spectra of aqueous solutions of alkalis, primarily the intense continuous absorption (CA) extending from 700 to 3600 cm^{-1} [24–27].

This CA of aqueous alkaline solutions was explained [24, 28] by the presence of $OH^- \cdot H_2O$ structural units with a short (R_{OO} ~ 2.6 Å) asymmetric superpolarizable H-bond:

$$H{-}O{-}H\cdots{}^{-}O{-}H \leftrightarrow H{-}O^{-}\cdots H{-}O{-}H.$$

According to our concept, the $OH^- \cdot H_2O$ structural unit formed in aqueous solutions of alkalis, is a stable species, more specifically, the $H_3O_2^-$ ion. This ion has a strong quasi-symmetric hydrogen bond, exhibits a characteristic IR spectrum [25, 26], and undergoes hydration due to the formation of H-bonds between its oxygen atoms and surrounding water molecules. The continuous absorption in the IR spectra of solutions containing $H_3O_2^-$ ions has the same nature as that in the spectra of other solutions containing species with bridges $(O\cdots H\cdots O)^{\pm}$. It consists of dozens of overlapping bands belonging to higher-order vibrations, at which the central proton shifts both along and across the H-bond. The high intensity of these vibrations is a consequence of their electrooptical anharmonicity and the symmetry of the bridge, whereas the large number of such vibrations is due to a strong kinematic interaction of the coordinates of the $O\cdots H\cdots O$ fragment with the internal coordinates of the $(RO\cdots H\cdots OR)^{\pm}$ ion [29–32]. The intensity of the CA is highest in the IR spectra of ions with symmetric hydrogen bridges; it decreases as the degree of their asymmetry increases [11, 30, 31].

Previously, we have studied IR spectra of aqueous solutions of NaOH and KOH over a frequency range of 1900 to 3800 cm^{-1} and found that, with increasing alkali concentration, the degree of hydration of $H_3O_2^-$ and the absorption coefficients in the CA range decrease [25, 26]. In these studies, a decrease in the absorption coefficient in the CA range for concentrated solutions has been formally attributed to an incomplete dissociation of the electrolytes. However, it was subsequently revealed that the absorption coefficients in the CA range of the IR spectra of solutions of acids depend on the degree of solvation of $(R_1O\cdots H\cdots OR_2)^+$ ions present in these solutions [15]. A similar effect is quite possible in alkaline solutions as well.

The aim of the present work was to study how the degree of hydration of $H_3O_2^-$ ions in aqueous solutions depends on the alkali concentration and the size of the cation. The objects of the study were $NaOH–H_2O$ and $KOH–H_2O$ solutions with a wide range of electrolyte concentrations. Solving the problem required (a) to examine how the IR spectra of aqueous NaOH and KOH solutions depend on their composition; (b) to perform quantum-chemical calculations of the characteristics of the $H_3O_2^-$ ion and its dihydrate; and (c) to interpret the IR spectra and analyze the spectral data by relying on calculation results.

EXPERIMENTAL

The stock aqueous NaOH and KOH solutions were prepared by dissolving reagent-grade solid alkalis in distilled water. Nearly saturated solutions were filtered through a Schott glass filter no. 4. The concentrations of the stock solutions were determined by titration with sulfuric acid in the presence of phenolphthalein indicator. Working solutions of required concentrations were prepared by weight-based dilution of the stock solution with distilled water.

The IR spectra of the aqueous NaOH and KOH solutions (900 to 2400 cm^{-1}) were recorded using a multiple frustrated total internal reflection (MFTIR) attachment with a Ge crystal having an incidence angle of 30° (number of reflections 8) at a temperature of 30°C, with the NaOH and KOH concentrations ranging within 0–47.8% and 0–51.95%, respectively. The effective thickness of the absorption layer at the frequency of 2000 cm^{-1} was 3.37 μm.

CALCULATION METHOD

The optimal structures, total energies, and vibrational spectra of the $H_3O_2^-$ ion (proton disolvate $(HO\cdots H\cdots OH)^-$) and its dihydrate were calculated by the GAUSSIAN-98 program [33] using density functional theory with the B3LYP functional in conjunction with the 6-31++G(d, p) basis set. An analysis of the found stationary points on the potential energy surface of the systems under study revealed that all of them are minima.

RESULTS AND DISCUSSION

Figure 1 shows IR spectra of aqueous KOH solutions over frequency ranges of 900–2400 cm^{-1} (this work) and 2400–3800 cm^{-1} ([25, 26]). With increasing alkali concentration, the spectra of the solutions exhibit significant changes: against the background of the weakening bands of water at 1640 and 3400 cm^{-1}, bands at 1030, 1130, 1920, and ~2900 cm^{-1}, together with long- and short-wavelength wings of the 1640 cm^{-1} band and intense CA within 900–3600 cm^{-1}, arise. The CA maximum is located near 2000 cm^{-1}. The observed changes in the spectra can be explained by the formation in the solutions of $H_3O_2^-$ ions with a strong quasi-symmetrical H-bond and by their subsequent hydration with water molecules [15, 34]. Note that the IR spectra of aqueous solutions of strong acids, in which $H_5O_2^+$ ions with a strong symmetrical H-bond are present, have a similar pattern.

The absorption bands in the measured IR spectra were interpreted using the results of quantum-chemical calculations for the $H_3O_2^-$ ion hydrated with two water molecules. A schematic picture of the optimized structure of the complex and its basic geometric parameters are displayed in the Scheme, whereas calculated frequencies of its normal vibrations and their assignments are given in Table 1. Table 1 also lists similar data for the isolated $H_3O_2^-$ ion and, for convenience of comparison, the frequencies of the maxima of the bands in the IR spectra of aqueous solutions of the alkalis.

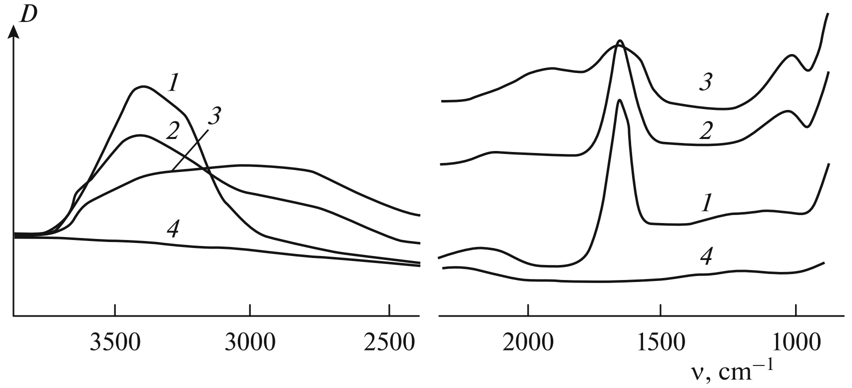
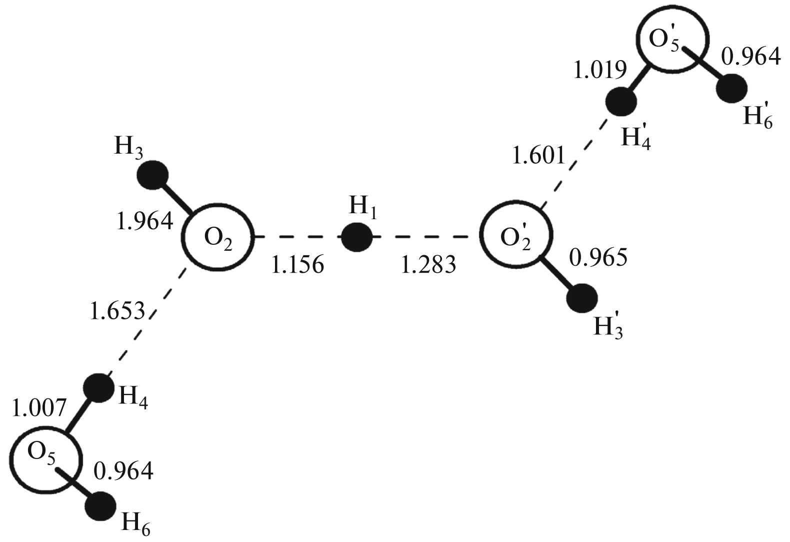


Fig. 1. MFTIR IR spectra of KOH aqueous solutions at $[KOH]_0$ (mol/L) = (*1*) 0, (*2*) 6.63, (*3*) 14.13, and (*4*) empty cell in frequency ranges of 900–2400 cm^{-1} (Ge, 30°, present work) and 2400–3800 cm^{-1} (Ge, 45° [26]).



Scheme.

Before comparing the calculated vibrational frequencies of the $H_3O_2^- \cdot 2H_2O$ complex with the experimental frequencies, it is important to emphasize the following. Our model takes into account only the interaction of the O2 and O2' proton-acceptor atoms of the $H_3O_2^-$ ion with the protons of the water molecules, since the H3 and H3' terminal hydrogen atoms (Scheme) do not form strong bonds with surrounding water molecules. This is evidenced by the 3600-cm^{-1} intense narrow line of the ν(O2–H3) and ν(O2'–H3') stretching vibrations observed in the Raman spectra of aqueous solutions of alkalis [2, 35]. In the IR spectra of these solutions, this vibration is less active and manifests itself in the form of a high frequency wing of the stretching vibration band of water molecules (Fig. 1).

According to the calculation, during antisymmetric stretching vibrations of the bridge bonds in the isolated $H_3O_2^-$ ion and its dihydrate, the proton shifts not only along the bridge, but also, to a lesser extent, in the perpendicular direction (angle γ changes). For brevity, this vibration will be denoted as ν_γ^{as}(O2···H1···O2').

As typical of “gas-phase” calculations simulating H-bonded molecular systems in solution, our calculation reproduced frequencies of a number vibrations with significant error ($\beta = (\nu^{exp} - \nu^{calc})/\nu^{exp}$, %). For the O2–H3 and O2'–H3' stretching vibrations, $\beta \leqslant 7.9\%$, whereas for the H1–O2'–H3' bending vibration, $\beta = 9.4\%$. The rest of the calculated vibrational frequencies of the complex $H_3O_2^- \cdot 2H_2O$ turned out to be in close agreement with the experimental values ($\beta = 0.6–3.4\%$) (Table 1), which makes it possible to assign the bands observed in the IR spectra of the NaOH and KOH aqueous solutions and provides an additional argument in favor of the formation of the $H_3O_2^- \cdot 2H_2O$ dihydrate, rather than its pyramidal

Table 1. Frequencies (ν, cm^{-1}), intensities of IR absorption (I, arb. units) and modes of the vibrations of the $H_3O_2^-$ ion and its dihydrate $H_3O_2^- \cdot 2H_2O$

ν^{exp}	$H_3O_2^-$		$H_3O_2^- \cdot 2H_2O$		Assignment of vibrations
	ν^{calc}	I	ν^{calc}	I	
<900	–	–	881 (I)	0.74	$(\gamma(\mathrm{O2\cdots H4\cdots O5}) + \gamma(\mathrm{O2'\cdots H4'\cdots O5'}))^{ap} + \nu_{\gamma}^{as}(\mathrm{O2\cdots H1\cdots O2'}) + \nu^{s}(\mathrm{O\cdots O})$
1030	1017	1.00	1046 (II)	0.32	$\nu_{\gamma}^{as}(\mathrm{O2\cdots H1\cdots O2'}) + (\gamma(\mathrm{O2\cdots H4\cdots O5}) + \gamma(\mathrm{O2'\cdots H4'\cdots O5'}))^{ip}$
1130	–	–	1122 (III)	1.00	$\nu_{\gamma}^{as}(\mathrm{O2\cdots H1\cdots O2'}) + (\gamma(\mathrm{O2\cdots H4\cdots O5}) + \gamma(\mathrm{O2'\cdots H4'\cdots O5'}))^{ap}$
~1600	1424	0.03	1449	0.04	$\delta(\mathrm{H1O2'H3'})$
	1659	0.01	1654	0.01	$\delta(\mathrm{H1O2'H3})$
1690	–	–	1701	0.04	$\delta(\mathrm{H4'O5'H6'})$
	–	–	1704	0.05	$\delta(\mathrm{H4O5H6})$
1920	–	–	~1927 ~2003 ~1965	– – –	I + II combination I + III combination Sum of (I + II) and (I + III) combinations
2270	–	–	2244	–	Overtone III
~2900	–	–	2868	0.92	$\nu(\mathrm{O5'{-}H4'})$
	–	–	3080	0.68	$\nu(\mathrm{O5{-}H4})$
3400	–	–	3869	0.01	$\nu(\mathrm{O5'{-}H6'})$
	–	–	3873	0.01	$\nu(\mathrm{O5{-}H6})$
3600	3808	0	3854	0	$\nu(\mathrm{O2'{-}H3'})$
	3833	0	3864	0	$\nu(\mathrm{O2{-}H3})$

γ and δ are the bending vibrations of the linear and nonlinear segments, respectively. The indices "s" and "as" designate the symmetric and asymmetric vibrations, whereas the indices "ip" and "ap" denote in-phase and anti-phase vibrations. For comparison with the listed data, the vibrational frequencies of the $OH^- \cdot (H_2O)_3$ complex higher than 600 cm^{-1} were calculated in the present work by density functional theory (B3LYP/6-31++G(d, p)): 1069, 1086, 1088, 1689, 1715, 2204, 2805, 2982, 3851, 3865 cm^{-1}.

conformer $OH^- \cdot 3H_2O$. Recall that the main feature indicative of the presence in aqueous alkaline solutions of ions with strong quasi-symmetric H-bonds is the manifestation of CA in the IR spectrum.

According to anharmonic [11] and quantum-chemical (Table 1) calculations, the most intense of the fundamental vibrations in the IR spectrum of the $H_3O_2^-$ ion is the vibration of the central proton along the hydrogen bridge $\left(\nu^{as}_{\mathrm{O\ldots H\ldots O}}\right)$. In the spectrum of the isolated $H_3O_2^-$ ion, its frequency is 1017 cm^{-1}. For the $H_3O_2^- \cdot 2H_2O$ dihydrate, this displacement of the proton takes place at two intense vibrations with noncharacteristic mode and occurs simultaneously with the displacements of the H4 and H4' atoms perpendicular to the H-bond (Table 1). Note a good agreement of the calculated frequencies of these vibrations (1046 and 1122 cm^{-1}) with experimental values (1030 and 1130 cm^{-1}). The spectrum of the trihydrate of the OH^- ion in the range under consideration features three vibrations with frequencies of 1069, 1086, and 1088 cm^{-1}. In the experiment, they should manifest themselves as a single absorption band.

The calculation results for the dihydrate ion strongly suggest that the absorption band at 1920 cm^{-1} (Fig. 1) belongs to combination vibrations (there are three possible interpretations). The arguments in favor of such an assignment are not only the frequencies of the intense fundamental vibrations, 881, 1046, and 1122 cm^{-1} (the sums of which are close to the frequency of the experimentally observed band), but also their modes (Table 1). The fact that each of these vibrations is accompanied by a shift of the central proton along and across the O···H···O bridge means that the respective combination vibrations must be intense in infrared absorption [11, 29–32]. In this spectral range, the spectrum of the OH^- ion trihydrate exhibits no bands corresponding to fundamental vibrations. Since this complex has no symmetrical H-bonds, it is unlikely that any of its combination or overtone vibrations are intense enough to be responsible for the absorption at the frequency of 1920 cm^{-1}.

In the range of bending vibrations of water molecules, the studied spectra (Fig. 1) feature absorption bands near 1600 and 1690 cm^{-1}, strongly overlapping with the 1640-cm^{-1} band. Judging from the calculation results, the first, low-frequency band of these bands is associated with the variations of ∠H1O2H3 and ∠H1O2'H3' angles in the $H_3O_2^-$ ion, whereas the second corresponds to the bending vibrations of the water molecules that hydrate it (Table 1) In the case of the $H_3O_2^- \cdot 2H_2O$ dihydrate, this band corresponds to the δ(H4O5H6) and δ(H4'O5'H6') vibrations (Scheme).

We began to analyze the experimental IR spectra from considering the concentration dependences of the optical density of the continuous absorption D_ν on [Na(K)OH] at frequencies of 970, 1300, 1400, 1920, 2000, 2200, and 2300 cm^{-1}. Figure 2 shows the data obtained for the frequency of 2000 cm^{-1}. In the range 0–5 mol/L, D_{2000} increases in proportion to the alkali concentration, with the CA coefficients ε_{2000} for both systems being the same, 131 L mol^{-1} cm^{-1}. For more concentrated solutions, the coefficient ε_{2000} decreases, and dependences *1* and *2* in Fig. 2, corresponding the NaOH and KOH solutions, diverge. Note that ε_{2000} decreases more significantly for NaOH solutions. For the NaOH solution most concentrated of the studied ([NaOH] = 17.9 mol/L), at a ratio of the concentrations of the analytical components of NaOH : H_2O = 1 : 2.24, ε_{2000} = 91 L mol^{-1} cm^{-1}. The same pattern of change of ε_{CA} was observed for the CA frequencies tested. That the value of ε_{CA} decreases for concentrated solutions reflects, in our view, the influence of the degree of hydration of $H_3O_2^-$ ions on their IR spectrum. Recall that, in the alkali concentration range of up to 5 mol/L, the solutions contain $H_3O_2^-$ ions fully hydrated by two water molecules [36]. A decrease in the degree of hydration of these ions leads to an increase in the degree of asymmetry of the O···H···O bridge, and consequently, to a decrease in the value of ε_{CA} [11, 30, 31].

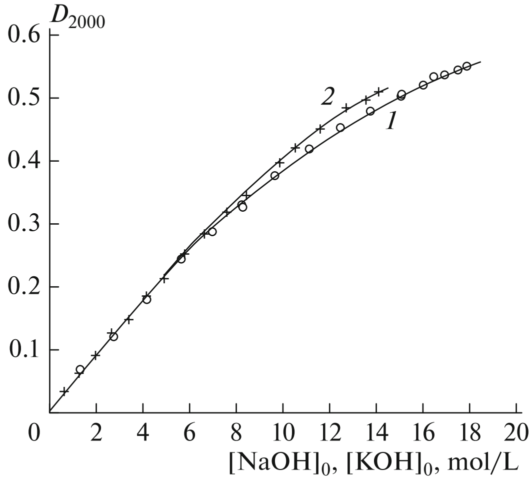


Fig. 2. Dependence of the optical density D_{2000} on the alkali concentration in (*1*) NaOH and (*2*) KOH aqueous solutions.

In [25, 26], the degrees of hydration of the $H_3O_2^-$ ion were obtained from data on the decrease in the optical density at 3400 cm^{-1} for NaOH and KOH solutions on the assumption that, at this frequency, the absorption belongs only to those water molecules that do not participate in the formation of $H_3O_2^-$ ions and in their hydration. However, it is known that the frequency of the stretching vibration of each of the OH groups of the water molecule in solution is determined mainly by the energy of H-bond involving the hydrogen atom of the given group, being weakly dependent on the strengths of the rest of the H-bonds formed by the molecule [37]. As applied to the molecules hydrating an $H_3O_2^-$ ion, this means that the vibrations of the bonds nearest to it, ν(O5–H4) and ν(O5'–H4') (their calculated frequencies are 2868 and 3080 cm^{-1}, respectively), can manifest themselves in experimental spectra as a band at 2900 cm^{-1} (Fig. 1), whereas the ν(O5–H6) and ν(O5'–H6') vibrations, interacting in solution with the water molecules can contribute to the absorption at 3400 cm^{-1}. Therefore, the data on the hydration numbers of $H_3O_2^-$ ions in NaOH and KOH aqueous solutions reported in [25, 26] need refinement.

In this paper, the hydration numbers of $H_3O_2^-$ ions were calculated based on the dependence of D_{2800} on the compositions of the NaOH–H_2O and KOH–H_2O solutions (Fig. 3). At the frequency of 2800 cm^{-1} (in contrast to 2900 cm^{-1}), the spectrum of pure water shows practically no absorption. For the solutions investigated, D_{2800}, as D_{CA} (Fig. 2), increases in proportion to the concentration of each of the alkali up to ~5–6 mol/L. In more concentrated solutions, the growth of D_{2800} slows down. The initial linear parts of the $D_{2800} = \varepsilon_{2800} l_{2800} \cdot 2[Na(K)OH]_0$ dependences yielded the absorption coefficients $\varepsilon_{2800} l_{2800}$ of water molecules that hydrate $H_3O_2^-$ ions in NaOH and KOH,

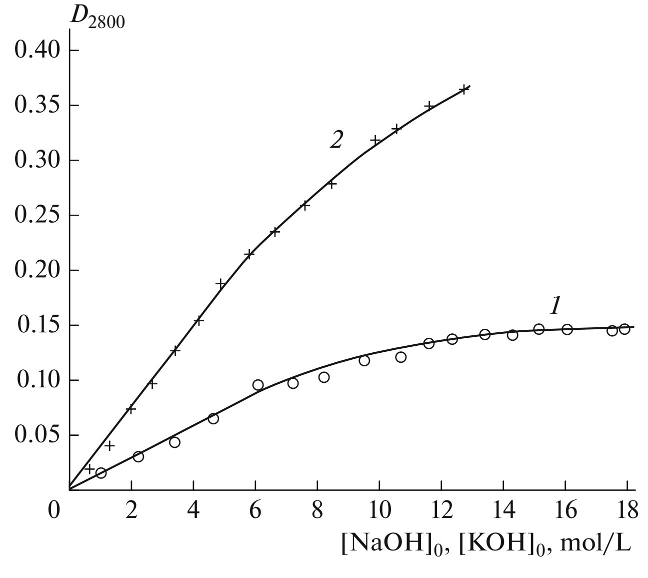


Fig. 3. Dependences of the optical density D_{2800} on the alkali concentration in (*1*) NaOH and (*2*) KOH aqueous solutions (data from [26]).

aqueous solutions, 7.40 × 10^{-3} and 1.86 × 10^{-2} L/mol, respectively.[1] The above formula takes into account that, in dilute solutions, each $H_3O_2^-$ ion is strongly hydrated by two water molecules. The obtained values of the coefficients were used to calculate the concentration of water molecules, $[H_2O]_{hydr}$, strongly hydrating $H_3O_2^-$ ions in more concentrated (>6 mol/L) NaOH and KOH solutions. The calculation results are presented in Tables 2 and 3. These tables also list the calculated (using $[H_2O]_{hydr}$) concentrations of $H_3O_2^-$ ions hydrated by one ($[H_3O_2^- \cdot H_2O]$) and two ($[H_3O_2^- \cdot 2H_2O]$) water molecules, the concentration of H_2O free molecules $[H_2O]_{free}$, and the concentration ratio $\alpha = [H_3O_2^- \cdot 2H_2O]/[Na(K)OH]_0$:

$$[H_2O]_{hydr} = 2[H_3O_2^- \cdot 2H_2O] + [H_3O_2^- \cdot H_2O],$$

$$[Na(K)OH]_0 = [H_3O_2^- \cdot 2H_2O] + [H_3O_2^- \cdot H_2O],$$

$$[H_2O]_{free} = [H_2O]_0 - [H_2O]_{hydr} - [Na(K)OH]_0.$$

Here, $[H_2O]_{free}$ is the concentration of water molecules that are not involved in the formation and strong hydration of $H_3O_2^-$ ions; $[H_2O]_0$ and $[Na(K)OH]_0$ are the stoichiometric concentrations of water and alkali in the solution.

Tables 2 and 3 show that the equilibrium

$$H_3O_2^- \cdot 2H_2O \leftrightarrow H_3O_2^- \cdot H_2O + H_2O \qquad \text{(I)}$$

begins to shift to the right when the solution still contains a large number of free water molecules.

This means that the monohydrate and cation compete for H_2O molecules. At $[NaOH]_0 = [KOH]_0$, the concentration of dihydrate, $[H_3O_2^- \cdot 2H_2O]$, in KOH solutions is higher than in NaOH solutions; i.e., in the presence of Na^+ cations equilibrium (I) is more significant shifted to the right than in the presence of K^+ cations. This explains why dependence *1* and *2* shown in Fig. 2 diverge. The observed effect is due to differences in the hydration of sodium and potassium cations, which correlates with the data on the size of the non-hydrated and hydrated Na^+ and K^+ ions [38].

The deviation from linearity in Fig. 2 is observed for solutions in which $H_3O_2^-$ ions firmly bound only with one water molecule appear, with a lower (compared to the dihydrate) absorption coefficient. Using the expression

$$D_\nu = \varepsilon_d l_\nu [H_3O_2^- \cdot 2H_2O] + \varepsilon_m l_\nu [H_3O_2^- \cdot H_2O], \qquad (1)$$

(ε_d and ε_m are the absorption coefficients of di- and mono-hydrated $H_3O_2^-$ ions), we calculated values of ε_m for solutions with NaOH and KOH concentrations above 6 mol/L at frequencies of 970, 1300, 1400, 1920, 2000, 2200, and 2300 cm^{-1}. The calculations were performed using $[H_3O_2^- \cdot 2H_2O]$ and $[H_3O_2^- \cdot H_2O]$ from Tables 2 and 3 and the CA coefficients ε_d obtained from the initial linear portions of dependences similar to those displayed in Fig. 2 for the frequency of 2000 cm^{-1}. The values of ε_d and ε_m are given in Table 4.

Based on the dependences of the coefficients ε_d and ε_m on the frequency, it is possible to obtain information on the CA profiles in the IR spectra of the $H_3O_2^- \cdot 2H_2O$ and $H_3O_2^- \cdot H_2O$ ions. Table 4 shows that the CA intensity for the monohydrate is lower than that for the dihydrate, a result that reflects a greater degree of asymmetry of the O···H···O central bridge of $H_3O_2^-$ ions strongly bound only with one water molecule.

An analysis of the CA IR spectra of the $H_3O_2^- \cdot H_2O$ monohydrate allowed us to reveal (1) the influence of the cation on the coefficient ε_m at the frequency of 970 cm^{-1}, (2) the dependence of ε_m on the alkali concentration at the frequencies of 1300 and 1400 cm^{-1}, and (3) the fact that the ratio $\varepsilon_d/\varepsilon_m$ at the frequency of 2300 cm^{-1} is markedly smaller than at the other frequencies.

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[1] The difference in the values of the coefficients $\varepsilon_{2800} l_{2800}$ is associated with the difference in the thicknesses of the absorbing layer for cells with Ge crystals with radiation incidence angles of 45° (NaOH) and 30° (KOH), equal to 0.93 and 2.41 μm, respectively. In this case, the values of ε_{2800} for both solutions are practically identical, 78.4 ± 1.2 L mol^{-1} cm^{-1}.

Table 2. Stoichiometric and equilibrium composition of NaOH aqueous solutions at 30°C

NaOH, %	$[NaOH]_0$	$[H_2O]_0$	$[H_2O]_{hydr}$	$[H_3O_2^- \cdot 2H_2O]$	$[H_3O_2^- \cdot H_2O]$	$[H_2O]_{free}$	α
	mol/L						
3.99	1.04	55.47	2.08	1.04	0	52.35	1
8.12	2.20	55.33	4.40	2.20	0	48.73	1
12.04	3.39	54.98	6.78	3.39	0	44.81	1
15.92	4.64	54.51	9.28	4.64	0	40.59	1
20.02	6.07	53.81	12.14	6.07	0	35.60	1
23.10	7.20	53.23	13.24	6.04	1.16	32.79	0.84
25.80	8.23	52.60	14.32	6.09	2.14	30.05	0.74
29.04	9.50	51.60	15.95	6.45	3.05	26.15	0.68
31.93	10.70	50.67	17.02	6.32	4.38	22.95	0.59
34.06	11.60	49.89	17.97	6.37	5.23	20.32	0.55
35.81	12.36	49.21	18.51	6.15	6.21	18.34	0.50
38.24	13.41	48.24	19.05	5.64	7.77	15.78	0.42
40.17	14.29	47.27	19.05	4.76	9.53	13.93	0.33
42.02	15.13	46.38	19.73	4.60	10.53	11.52	0.30
43.96	16.05	45.39	19.73	3.68	12.37	9.61	0.23
45.93	16.97	44.37	19.45	2.48	14.49	7.95	0.15
47.04	17.50	43.75	19.59	2.09	15.41	6.66	0.12
47.84	17.90	43.32	19.73	1.83	16.07	5.69	0.10

Table 3. Stoichiometric and equilibrium composition of KOH aqueous solutions at 30°C

KOH, %	$[KOH]_0$	$[H_2O]_0$	$[H_2O]_{hydr}$	$[H_3O_2^- \cdot 2H_2O]$	$[H_3O_2^- \cdot H_2O]$	$[H_2O]_{free}$	α
	mol/L						
3.53	0.65	54.99	1.30	0.65	0	53.04	1
6.93	1.31	54.71	2.62	1.31	0	50.78	1
10.18	1.98	54.27	3.96	1.98	0	48.33	1
13.32	2.65	53.79	5.30	2.65	0	45.84	1
16.59	3.40	53.20	6.80	3.40	0	43.00	1
19.78	4.16	52.50	8.32	4.16	0	40.02	1
22.69	4.89	51.84	9.78	4.89	0	37.17	1
26.24	5.81	50.89	11.62	5.81	0	33.46	1
29.23	6.63	50.00	12.58	5.95	0.68	30.79	0.90
32.61	7.61	48.96	13.87	6.26	1.35	27.48	0.82
35.41	8.45	48.00	14.95	6.50	1.95	24.60	0.77
39.86	9.87	46.30	17.10	7.23	2.64	19.33	0.73
41.96	10.55	45.46	17.63	7.08	3.47	17.28	0.67
45.05	11.61	44.10	18.71	7.10	4.51	13.78	0.61
48.14	12.72	42.66	19.57	6.85	5.87	10.37	0.54
50.44	13.56	41.48	20.22	6.66	6.90	7.70	0.49
51.95	14.13	40.70	20.70	6.57	7.56	5.87	0.46

Table 4. Values of the coefficients ε_d и ε_m in formula (1) for the CA frequencies in the IR spectra of aqueous solutions of NaOH and KOH at 30°C

ν, cm^{-1}	ε_d	ε_m	$\varepsilon_d/\varepsilon_m$
	L mol^{-1} cm^{-1}		
970	52	34 (NaOH) 41 (KOH)	1.53(NaOH) 1.27 (KOH)
1300	69	25(dil)* 40(conc)**	2.76(dil)* 1.72(conc)**
1400	76	35(dil)* 45(conc)**	2.17(dil)* 1.69(conc)**
1920	135	86	1.57
2000	131	87	1.50
2200	119	81	1.47
2300	114	91	1.25

For the NaOH и KOH solutions, the values of ε_d are identical for all the frequencies, whereas the values of ε_m, for all the frequencies except 970 cm^{-1}; dil and conc denote dilute and concentrated solutions.

* The values ε_m and $\varepsilon_d/\varepsilon_m$ correspond to [NaOH] from 7.2 to 12.36 mol/L and [KOH] from 6.63 to 11.61 mol/L.

** The values of ε_m and $\varepsilon_d/\varepsilon_m$ correspond to [NaOH] from 16.05 to 17.90 mol/L.

For all the frequencies except 970 cm^{-1}, the values of ε_m turned out to be virtually the same for the NaOH and KOH solutions irrespective of their concentrations. At 970 cm^{-1}, the value of ε_m for the KOH solutions turned out to be ~20% higher than that for the NaOH solutions. Note that this frequency corresponds to a minimum between two intense absorption bands. The first of them, ν_γ^{as}(O2···H1···O2'), is a spectral manifestation of the $H_3O_2^-$ ion, whereas the second band corresponds to a complex-mode vibration (Table 1), being characteristic only for its dihydrate. Therefore, the contribution to the measured value of D_{970} from the high-frequency wing of this band (due to objective reasons not taken into account when calculating the relevant value of ε_m) should vary symbatically with the $H_3O_2^- \cdot 2H_2O$ concentration. Tables 2 and 3 shows that, at an equal concentration of $H_3O_2^-$ ions ($[NaOH]_0 = [KOH]_0$), the concentration of $H_3O_2^- \cdot 2H_2O$ in the KOH solutions is significantly higher than in the NaOH solution, which explains the observed dependence of ε_m on the type of cation at the frequency of 970 cm^{-1}.

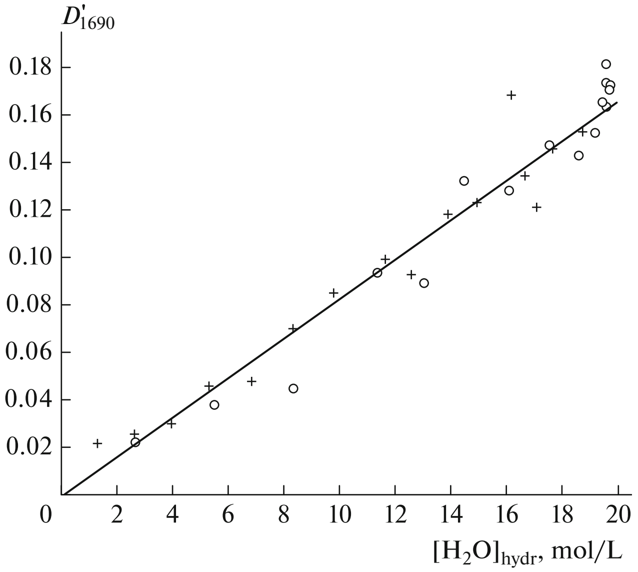

Fig. 4. Dependence of the optical density D'_{1690} on $[H_2O]_{hydr}$ in aqueous solutions of (circle) NaOH and (cross) KOH.

At frequencies above 1900 cm^{-1}, ε_m is constant within better than 10% over the entire range of NaOH and KOH concentrations covered. At both 1300 and 1400 cm^{-1}, ε_m is constant for relatively dilute solutions of NaOH and KOH (ε_m (dil)) and for the most concentrated NaOH solutions (ε_m(conc)), with ε_m(dil) < ε_m(conc) (Table 4). The difference in the values of these coefficients for each of the frequencies exceeds the possible error of their determination (10%). The observed effect can be explained by the influence of the cation on the symmetry of the OHO bridge in the $H_3O_2^- \cdot H_2O$ monohydrate. That the coefficient ε_m(conc) is higher than ε_m(dil) is indicative of a greater degree of symmetry of the OHO bridge in $H_3O_2^- \cdot H_2O$ ions in concentrated NaOH solutions.

Within 1900–2200 cm^{-1}, the $\varepsilon_d/\varepsilon_m$ ratio is approximately constant, ~1.5. The $\varepsilon_d/\varepsilon_m$ ratio at 2300 cm^{-1} is significantly smaller, 1.25. This result can be explained by the fact that, near this frequency, there is a band with the maximum at 2270 cm^{-1} [39].

The bending vibrations of the water molecules that hydrate $H_3O_2^-$ ions are observed at frequencies above 1640 cm^{-1}, in particular, the δ(H4O5H6) and δ(H4'O5'H6') vibrations for the dihydrate (Scheme). Let the optical density of these vibrations for the terminal water molecules of the mono- and dihydrate of the $H_3O_2^-$ ion be D'_ν. According to calculations, the maxima of the corresponding bands are located within 1690–1705 cm^{-1}, i.e., in the long-wavelength wing of the δ(HOH) band of free water molecules. Figure 4 shows how D'_{1690} depends on the concentration $[H_2O]_{hydr}$ of water molecules hydrating $H_3O_2^-$ ions in NaOH and KOH solutions. The values of D'_{1690} were obtained by subtracting the contribution from the absorption of free water molecules $[H_2O]_{free}$ at this frequency from the measured values of D_{1690}: $D'_{1690} = D_{1690} - \varepsilon_{H_2O} l_{1690}[H_2O]_{free}$. The concentrations $[H_2O]_{free}$ are listed in Tables 2 and 3, whereas the absorption coefficient $\varepsilon_{H_2O} l_{1690}$ was obtained from the spectrum of pure water. Note that the D'_{1690} versus $[H_2O]_{hydr}$ dependence is common for the NaOH and KOH solutions. This dependence is linear, i.e., the values of the absorption coefficients of bending vibrations of the water molecules that make up the mono- and dihydrates of $H_3O_2^-$ ions are similar.

As noted above, the IR spectra of the NaOH and KOH aqueous solutions feature a number of bands against the background of the CA, which can be assigned to the fundamental vibrations of the $H_3O_2^-$ ion. According to calculations, the band with the maximum at 1030 cm^{-1} belongs to a complex-mode vibration, with the main contribution to it coming from the displacement of the central proton in the O···H···O bridge of the $H_3O_2^-$ ion (Table 1). Let us examine how the absorption coefficient at this frequency depends on the degree of hydration of the $H_3O_2^-$ ion. Figure 5a displays the dependence of D_{1030} on the concentration $[Na(K)OH]_0$. The optical density D_{1030} does not depend on the type of alkali cation and increases linearly with $[Na(K)OH]_0$ up to ~5 mol/L. At higher solution concentrations, the growth of D_{1030} slows down; i.e., changes similar to those in the CA take place. This behavior is consistent with the CA formation model proposed in [11, 29–32]. The decrease in the absorption coefficient ε_{1030} can be accounted for by a lower symmetry of the O···H···O central fragment in the $H_3O_2^- \cdot H_2O$ monohydrate as compared to the $H_3O_2^- \cdot 2H_2O$ dihydrate.

As discussed above, the low frequency wing of the 1640 cm^{-1} band in the IR spectra of the aqueous alkaline solutions features an additional band, which, according to the calculations, belongs to the δ(H1O2H3) and δ(H1'O2'H3') vibrations of the fragments of the $H_3O_2^-$ ion (Scheme). The dependences of the optical density of this band on the compositions of the solutions were analyzed at two frequencies, 1600 cm^{-1} (near its expected maximum) and 1550 cm^{-1} (where there is no absorption of free water molecules). These dependences are shown in Figs. 5b and 5c. The values of D'_{1600} were calculated in the same manner as those of D'_{1690}, i.e., by subtracting the absorption of free water molecules from the experimental values of D_{1600}. It is evident that the behavior of these dependences is essentially the same. For all the solutions, except for the most concentrated solutions of NaOH, the optical densities D'_{1600} and D_{1550} increases in proportion to the

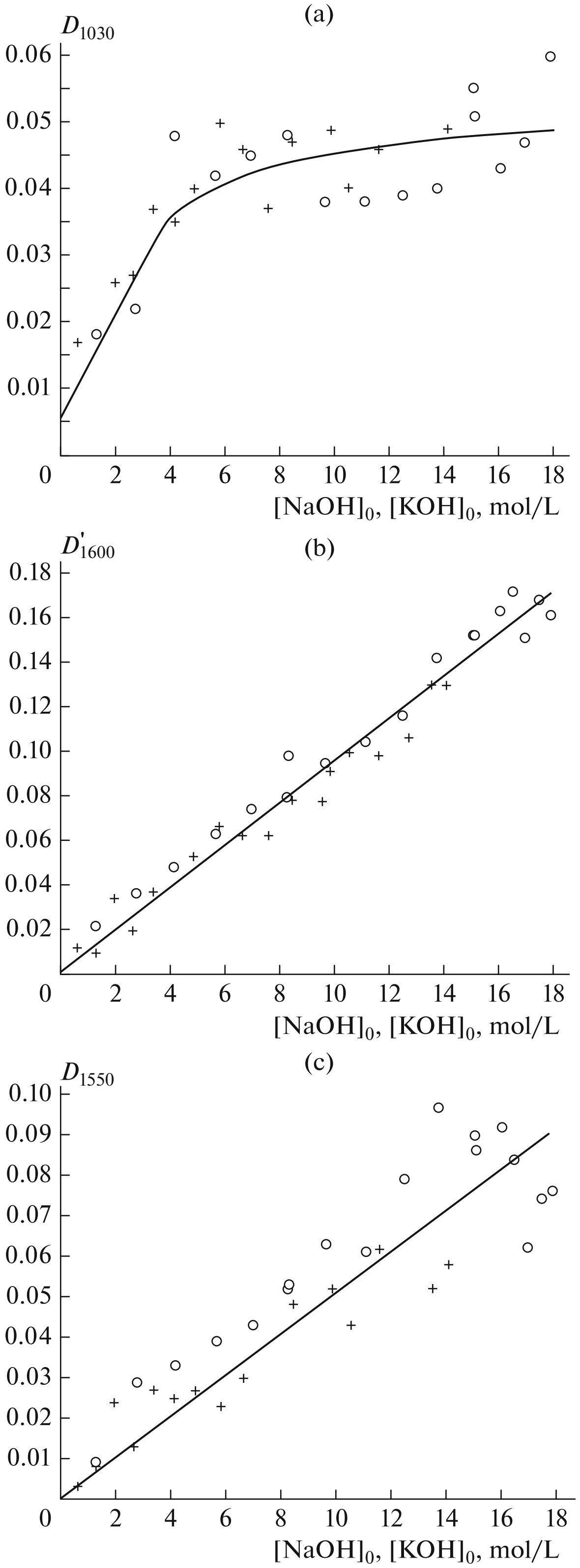

Fig. 5. Dependence of the optical densities D_ν on the alkali concentration in ([circle]) NaOH and ([cross]) KOH aqueous solutions at frequencies ν (in cm^{-1}) of (a) 1030 (b) 1600, and (c) 1550. At the frequency of 1030 cm^{-1}, the absorption of pure water of the spectrum is nonzero.

NaOH or KOH concentration. The influence of the cation on the course of curves in Figs. 5b and 5c is not observed.

Calculations suggest that the 1920-cm^{-1} band in the IR spectra of NaOH and KOH aqueous solutions belongs to combination vibrations of the $H_3O_2^-$ ion. In this case, with increasing alkali concentration, the optical density D_{1920} should vary so as do the optical densities of the CA at the nearby frequencies 2000 and 2200 cm^{-1}, which is really observed. According to Table 4, the ratio of the absorption coefficients of the $H_3O_2^- \cdot 2H_2O$ dihydrate ε_d and $H_3O_2^- \cdot H_2O$ monohydrate ε_m at frequencies 1920, 2000, and 2200 cm^{-1} are approximately the same.

Thus, the changes in the IR spectra of NaOH and KOH aqueous solutions occurring with increasing alkali concentrations can be explained by the formation of $H_3O_2^-$ ions with a quasi-symmetrical strong hydrogen bond and their subsequent hydration by one or two water molecules. The effect of the cation nature on the degree of hydration of the ion was observed. The equilibrium concentrations of the monohydrate ($H_3O_2^- \cdot H_2O$) and dihydrate ($H_3O_2^- \cdot 2H_2O$) were calculated, and their CA IR spectra were isolated. Interpretation of the IR spectra and analysis of the spectral data were performed based on the results of quantum-chemical calculations of the characteristics of the free and hydrated $H_3O_2^-$ ion.

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