

Modeling the Hydration and Proton Transport in Solid Electrolytes Based on Phenolsulfonic Acids*

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Abstract—Geometrical and energetic characteristics of crystal hydrates of individual aromatic sulfonic acids and their complexes with poly(vinyl alcohol) as well as the paths for the proton transport in them are calculated in the framework of the density functional theory (version B3LYP) employing the 6-31G** basis set. The energy of attachment of water to *ortho*-substituted aromatic sulfonic acids is demonstrated to diminish from 74.4 to 54.8 kJ mol⁻¹ in the following series of substituents: -OH, -F, -CH₃, -H, -Cl, and -COOH. For the dimers that comprise individual phenolsulfonic acids, the energy of attachment of one water molecule to the SO₃H group is estimated to be equal to 92–105 kJ mol⁻¹. In the dimers comprising individual phenolsulfonic acids, the specific energy of intermolecular bonds (bond energy per monomer molecule) is found to be equal to 49.3 and 58.5 kJ mol⁻¹ for, respectively, phenol-2,4-disulfo and phenol-2-sulfo acids. During the formation of polymer membranes based on poly(vinyl alcohol) and phenolsulfonic acids, it is energetically favorable that at least one water molecule should remain in the vicinity of the SO₃H fragment. According to the calculations, the proton migration along the SO₃H group in anhydrous environment is hampered by a barrier of 125–132 kJ mol⁻¹. In the presence of water, the proton conductivity is of a relay character, with an activation barrier equal to 21–33 kJ mol⁻¹. The latter value is close to experimental data (17–25 kJ mol⁻¹).

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Key words: aromatic sulfonic acids, hydrogen bonds, proton conductivity, density functional (B3LYP) calculation

INTRODUCTION

Due to their low working temperature and high efficiency, fuel cells are viewed as most promising for the energy production out of hydrogen-containing fuel, especially in portable and mobile devices. The last few years marked a steady tendency toward transition from classic fuel cells with liquid electrolytes to completely solid-state fuel cells and, for portable current sources, from high- to low-temperature cells all over the world. The low-temperature fuel cells as a rule make use of polymer membranes based on Nafion, but these materials must work in conditions of permanent thermo- and hydrostaticing [1]. As follows from the literature data, the most “narrow” places in such constructions are both the membranes themselves and the techniques used for commutating the membranes with the rest of the fuel cell components. As a special group of proton-exchange membranes that has actively been developed

of late one can single out materials where conductivity is realized at the expense of dissociation of low-molecular-weight compounds in a solvent that is inserted into a polymer matrix. For example, the insertion of strong organic acids (fluoroacetic acid, sulfonic acids, and so on) into the composition of Nafion-like or sulfonated polymers leads to that the effective proton transport is realized in wider intervals of the temperature and humidity of the environment [2].

The systems poly(vinyl alcohol) (PVA)–acid served as a basis for the production of a series of proton-conductive membranes that are capable of prolonged efficient operation in the composition of fuel cells in wide intervals of the temperature and humidity of the environment, which gives one a chance to create fuel cells working in natural conditions on the Earth without thermostating or humidification. The specific conductivity of such membranes in all conditions studied is greater than the specific conductivity of Nafion [3].

As we have mentioned in the foregoing, the insertion of organic and inorganic acids into the composition

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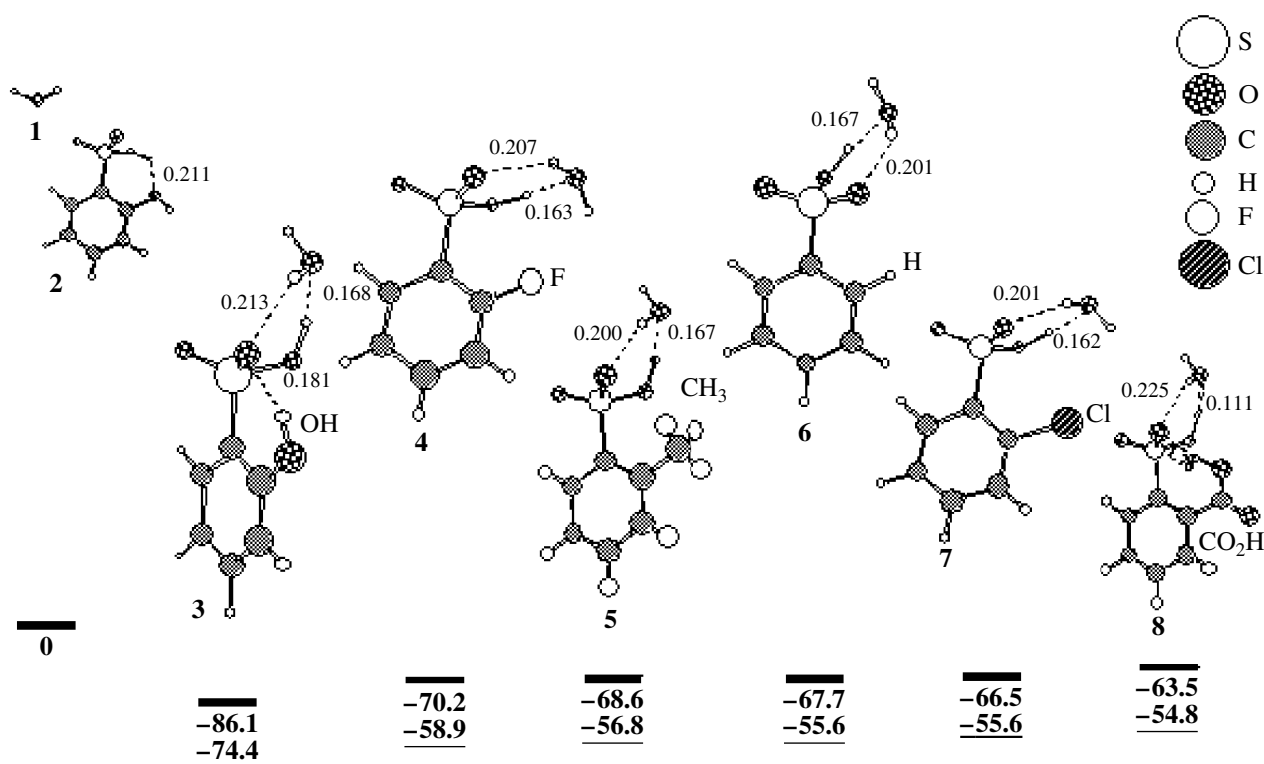


Fig. 1. Energetic scheme illustrating the formation of structures of individual sulfonic acids with different *o*-substituents. Numbers in the figure mark the most substantial distances between atoms (expressed in units of nm) and relative energies of isomers (in kJ mol^{-1}) calculated with allowance (underlined values) and without allowance (not underlined values) made for the energy of zero vibrations (ZPE).

of a polymer electrolyte leads to an improvement in thermal and mechanical characteristics as well as to that the effective proton transport is realized in wider intervals of the temperature and humidity of the environment. However, it is difficult to understand the proton transport mechanism in the systems that were obtained, for the molecular structure of the inserted additive, for example an aromatic sulfonic acid, is frequently unknown. This is connected with the difficult task of isolating compounds of this particular class in the form of single crystals, which is hampered by a strong dependence of an aggregate state of sulfonic acids on the humidity of the environment and, correspondingly, on the compound hydration degree. Owing to the presence of intra- and intermolecular hydrogen bonds as well as to a high degree of ionization of available sulfonate groups in the presence of water, the benzenepolysulfonic acids are good model systems for elucidating the migration paths of protons in crystalline structures. Hydrates of aromatic sulfonic acids are of special interest also from the viewpoint of investigation of more highly hydrated forms of the proton in a crystalline state [4–6].

In order to understand the structure of proton-conductive polymer membranes and the proton transport

mechanism in them, there was performed a quantum-chemical calculation of individual aromatic sulfonic acids with different substituents in the *ortho*-position, phenoldisulfonic acids with different position of one of the SO_3H groups, and intermolecular oligomer complexes based on PVA and phenolsulfonic acids (PSA).

EXPERIMENTAL

A quantum-chemical simulation. The PVA ($[-\text{CH}_2-\text{CH}(\text{OH})-]_n$) + PSA [$\text{C}_6\text{H}_{6-1-n}(\text{OH})(\text{SO}_3\text{H})_n$] system under consideration was simulated by clusters that are presented in Figs. 1–6. The calculations of geometrical parameters and thermodynamic stability of different isomers were conducted with use made of the density functional theory DFT with the hybrid functional B3LYP [7] employing the 6-31G** basis set. Program package Gaussian-03 was used to perform the calculations [8]. In the course of the present investigation there was performed a complete optimization of the geometrical and energetic characteristics pertaining to the molecules under consideration. The optimization was carried out in the framework of the above-specified basis set and the calculation method. Figures 1–6 show structures of calculated molecules, most substantial

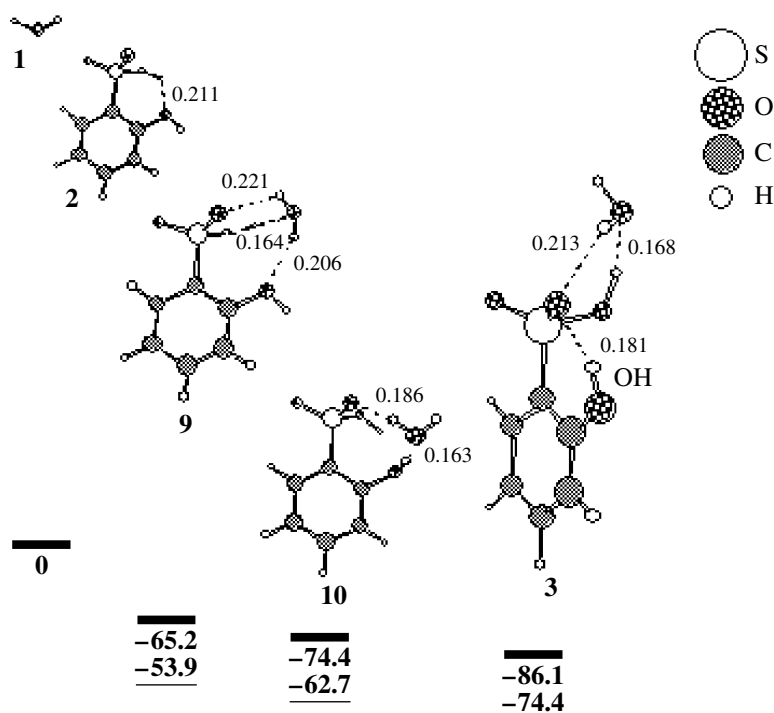


Fig. 2. Energetic scheme illustrating the formation of hydrates of phenolsulfonic acid. Numbers in the figure mark the most substantial distances between atoms (expressed in units of nm) and relative energies of isomers (in kJ mol⁻¹) calculated with allowance (underlined values) and without allowance (not underlined values) made for the energy of zero vibrations (ZPE).

distances between atoms, and relative energies of isomers with and without allowance for the energy of zero vibrations (ZPE).

Measurements of conductivity. To measure conductivity by the method of impedance spectroscopy, symmetrical cells Pt/compound/Pt were used. The cells were pressed under a pressure of 30 MPa and were continuously evacuated or kept at a certain value of humidity of the surrounding environment. The frequency dependences of the resistance of specimens were obtained on an LCR-819 impedancemeter of the firm Goodwill Instrument in the frequency interval extending from 12 Hz to 100 kHz as well as on an Elins Z-350 M impedancemeter, in the frequency region 0.1 Hz to 1.5 MHz. The frequency dependences of the resistance was analyzed by a graph-analytic method [9].

RESULTS OF CALCULATIONS

Aromatic Sulfonic Acids with Different Substituents in the o-Position

Most aromatic sulfonic acids are known to retain crystalline water sufficiently strongly [4–6]. This creates prerequisites for the proton transport in broad ranges of temperature and relative humidity.

As to our work, its aim was to simulate geometrical and energetic characteristics of crystal hydrates of substituted benzenesulfonic acids and their complexes with PVA as well as the paths for proton transport in systems under investigation. In connection with this, the goal of the first stage of calculations was to elucidate a dependence of the strength of the bond between derivatives of monobenzenesulfonic acids with different substituents in the *ortho*-position and water molecules. For the substituents we selected –OH, –F, –CH₃, –H, –Cl, and –COOH. The energy of attachment of a water molecule to a monobenzenesulfonic acid with different substituents (for example, **1** + **2** → **3**, Fig. 1) decreases in the series of *ortho*-substituents OH (**3**), F (**4**), CH₃ (**5**), H (**6**), Cl (**7**), and COOH (**8**) from 74.4 to 54.8 kJ mol⁻¹ (Fig. 1).

According to the results yielded by the calculations, crystal hydrate of *ortho*-phenolsulfonic acid (p-2-sa) happened to be most stable (Figs. 1, 2; isomer **3**; 74.4 kJ mol⁻¹). Therefore, possible isomers of that compound were simulated. In the case of p-2-sa there are possible three versions of the attachment of a water molecule, specifically, isomers **3**, **9**, and **10** (Fig. 2). The isomers in which water is bonded simultaneously with one oxygen atom of the SO₃H group and the

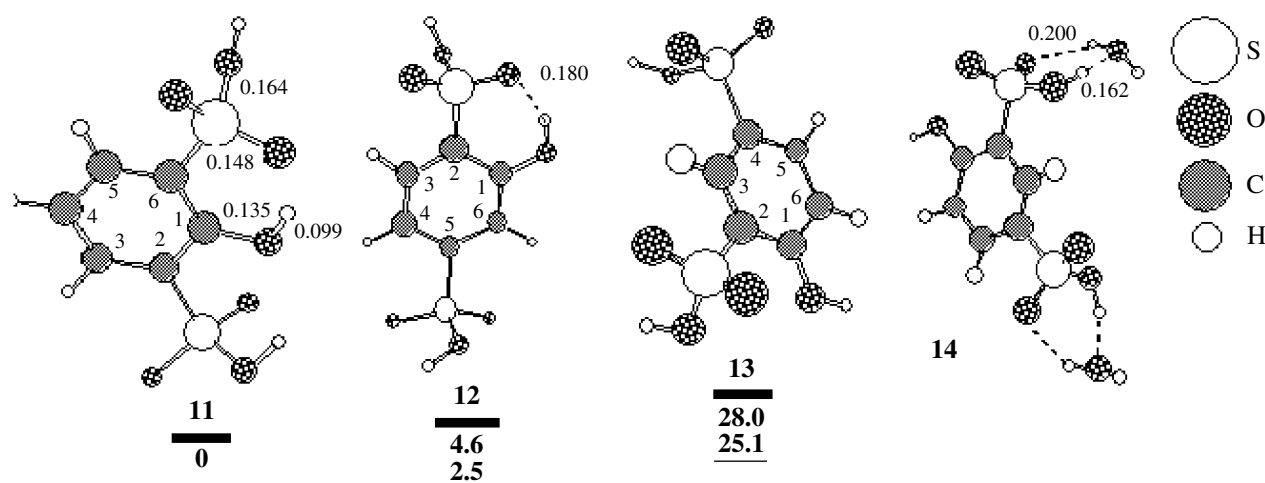


Fig. 3. Energetic scheme illustrating the formation of structures of various phenoldisulfonic acids. Numbers in the figure mark the most substantial distances between atoms (expressed in units of nm) and relative energies of isomers (in kJ mol^{-1}) calculated with allowance (underlined values) and without allowance (not underlined values) made for the energy of zero vibrations (ZPE).

hydrogen of the OH group (**10**) or water is simultaneously bonded with atoms of oxygen and hydrogen of the SO_3H group and the oxygen atom of the OH group (**9**) lie in the energy scale by, respectively, 11.7 and 20.5 kJ mol^{-1} higher than isomer **3**, in which water is bonded solely with atoms of oxygen and hydrogen of the SO_3H group.

As follows from the results yielded by the calculations, the maximum contribution to the energy of the water interaction with compounds under investigation is made by sulfonate groups. In connection with this, the task of the next stage of work was to simulate the behavior of isomers of phenoldisulfonic acids with water.

Phenoldisulfonic Acids

Figure 3 presents calculated structures of isomers of the following phenoldisulfonic acids: p-2,6-dsa (**11**), p-2,5-dsa (**12**), and p-2,4-dsa (**13**). Isomer **11** is most stable energetically. Isomer **12** is situated in the energy scale by 2.5 kJ mol^{-1} higher. Isomer **13** is situated still higher by another 22.6 kJ mol^{-1} .

According to the calculations, in the presence of water at the expense of the formation of hydrogen bonds energetically favorable is the unification of several molecules of PSA and water. In the table we present the calculated energies for processes of interaction between molecules of sulfonic acids and water. The numbering of the structures in the table corresponds to the numbering in the figures. When calculating the formation energy, the energy is given as calculated per monomer molecule (specific energy).

We infer from the table that the interaction between p-2-sa (**2**) and a water molecule with the formation of hydrate p-2-sa as a half of dimer **15** is energetically favorable by $103.7 \text{ kJ mol}^{-1}$ (Figs. 2, 4; table, scheme 1).

The interaction between p-2,5-dsa (**12**) and a water molecule with the formation of hydrate p-2,5-dsa as a half of dimer **16** is energetically favorable by 94.9 kJ mol^{-1} (Figs. 3, 4; table, scheme 1).

The attachment of two water molecules to monomer p-2,4-dsa (**13**) with the formation of dihydrate p-2,4-dsa (**14**) is energetically favorable by $108.3 \text{ kJ mol}^{-1}$ (Fig. 3; table, scheme 7). The exothermicity of processes of interaction between p-2,4-dsa (**13**) and one water molecule with the formation of monohydrate p-2,4-dsa as a half of dimer **17** (scheme 4) and the interaction of p-2,4-dsa (**13**) with two water molecules with the formation of dihydrate p-2,4-dsa as a half of dimer **18** (Figs. 3, 4; table, scheme 3) is equal to 80.3 and $180.6 \text{ kJ mol}^{-1}$, respectively.

Thus, the energy of attachment of one water molecule to one SO_3H group in a dimer may be estimated as 79–92, 94.9, and $103.7 \text{ kJ mol}^{-1}$ for, respectively, p-2,4-dsa, p-2,5-dsa, and p-2-sa. The dimerization energy per monomer molecule is equal to 49.3, and 58.5 kJ mol^{-1} for **18** and **15** (Fig. 4; table, schemes 6 and 2).

According to the calculations, the formation of tetramer **19** during the interaction of two dimers **18** is energetically favorable by $174.3 \text{ kJ mol}^{-1}$ (Fig. 4; table, scheme 10). During the interaction of four monomers **14**, the formation of tetramer **19** is favorable by 93.2 kJ mol^{-1} , as calculated per monomer (table, scheme 8), in so doing, there emerges a possibility of a link between fragments through the oxonium ion H_3O^+

Relative energies required for the formation of various isomers out of fragments. In parentheses we give values that were calculated with allowance made for the energy of zero vibrations. The minus sign implies that the full energy diminishes as a result of the reaction, i.e. the reaction is exothermic and the energy is released in the course of the reaction. The plus sign indicates endothermicity of the reaction

Scheme no.	Molecules, fragmentation, and defragmentation	Reaction scheme	ΔE , kJ mol ⁻¹
1	$p\text{-}2\text{-sa} + \text{H}_2\text{O} \longrightarrow 1/2(p\text{-}2\text{-sa} \cdot \text{H}_2\text{O})_2$	$\mathbf{2} + \mathbf{1} \longrightarrow 1/2 \cdot \mathbf{15}$	-116.6 (-103.7)
2	$p\text{-}2\text{-sa} \cdot \text{H}_2\text{O} \longrightarrow 1/2(p\text{-}2\text{-sa} \cdot \text{H}_2\text{O})_2$	$\mathbf{3} \longrightarrow 1/2 \cdot \mathbf{15}$	-61 (-58.5)
3	$p\text{-}2,4\text{-dsa} + 2\text{H}_2\text{O} \longrightarrow 1/2(p\text{-}2,4\text{-dsa} \cdot 2\text{H}_2\text{O})_2$	$\mathbf{13} + \mathbf{1} + \mathbf{1} \longrightarrow 1/2 \cdot \mathbf{18}$	-180.6
4	$p\text{-}2,4\text{-dsa} + \text{H}_2\text{O} \longrightarrow 1/2(p\text{-}2,4\text{-dsa} \cdot \text{H}_2\text{O})_2$	$\mathbf{13} + \mathbf{1} \longrightarrow 1/2 \cdot \mathbf{17}$	-92.8 (-80.3)
5	$p\text{-}2,5\text{-dsa} + \text{H}_2\text{O} \longrightarrow 1/2(p\text{-}2,5\text{-dsa} \cdot \text{H}_2\text{O})_2$	$\mathbf{12} + \mathbf{1} \longrightarrow 1/2 \cdot \mathbf{16}$	-94.9
6	$p\text{-}2,4\text{-dsa} \cdot 2\text{H}_2\text{O} \longrightarrow 1/2(p\text{-}2,4\text{-dsa} \cdot 2\text{H}_2\text{O})_2$	$\mathbf{14} \longrightarrow 1/2 \cdot \mathbf{18}$	-49.3
7	$p\text{-}2,4\text{-dsa} + 2\text{H}_2\text{O} \longrightarrow p\text{-}2,4\text{-dsa} \cdot 2\text{H}_2\text{O}$	$\mathbf{13} + \mathbf{1} + \mathbf{1} \longrightarrow \mathbf{14}$	-131.3 (-108.3)
8	$p\text{-}2,4\text{-dsa} \cdot 2\text{H}_2\text{O} \longrightarrow 1/4(p\text{-}2,4\text{-dsa} \cdot 2\text{H}_2\text{O})_4$	$\mathbf{14} \longrightarrow 1/4 \cdot \mathbf{19}$	-93.2
9	$p\text{-}2,4\text{-dsa} + 2\text{H}_2\text{O} \longrightarrow 1/4(p\text{-}2,4\text{-dsa} \cdot 2\text{H}_2\text{O})_4$	$\mathbf{13} + \mathbf{1} + \mathbf{1} \longrightarrow 1/4 \cdot \mathbf{19}$	-224
10	$(p\text{-}2,4\text{-dsa} \cdot 2\text{H}_2\text{O})_2 \longrightarrow 1/2(p\text{-}2,4\text{-dsa} \cdot 2\text{H}_2\text{O})_4$	$\mathbf{18} \longrightarrow 1/2 \cdot \mathbf{19}$	-174.3
11	$\text{PVA} + p\text{-}2,6\text{-dsa} \longrightarrow \text{PVA} \cdot p\text{-}2,6\text{-dsa} + \text{H}_2\text{O}$	$\mathbf{20} + \mathbf{11} \longrightarrow \mathbf{24} + \mathbf{1}$	26.8 (19.2)
12	$\text{PVA} + p\text{-}2,6\text{-dsa} \longrightarrow \text{PVA} \cdot p\text{-}2,6\text{-dsa} \cdot \text{H}_2\text{O}$	$\mathbf{20} + \mathbf{11} \longrightarrow \mathbf{28}$	-49.7
13	$\text{PVA} + p\text{-}2,6\text{-dsa} \longrightarrow \text{PVA} \cdot p\text{-}2,6\text{-dsa} \cdot \text{H}_2\text{O}$	$\mathbf{20} + \mathbf{11} \longrightarrow \mathbf{29}$	-61.4 (-49.7)
14	$\text{PVA} \cdot p\text{-}2,6\text{-dsa} + \text{H}_2\text{O} \longrightarrow \text{PVA} \cdot p\text{-}2,6\text{-dsa} \cdot \text{H}_2\text{O}$	$\mathbf{30} + \mathbf{1} \longrightarrow \mathbf{31}$	-79.8 (-69.8)

(Fig. 4), which leads to a sharp increase in the energy of detachment of a water molecule from the acid in the tetramer. The energy of detachment of two water molecules from the acid fragment in tetramer **19** is equal to 224 kJ mol⁻¹ (table, scheme 9), correspondingly, 112 kJ mol⁻¹ go to one water molecule. In the calculation, benzene rings of the first and second monomer fragments of tetramer **19** lie in parallel planes at a distance of 0.59 nm. Geometrical parameters of the calculated tetramer are close to those obtained as a result of an x-ray diffraction analysis of single-crystal dihydrate of phenol-2,4-disulfo acid [9]. The C–C distances in the benzene ring are equal to 0.1390–0.1409 nm. The S–O distances in sulfonate groups do not exceed 0.1479–

0.1503 nm, which coincides with the X-ray data reported in [10] to within 0.002–0.004 nm. The OH group is situated in the plane of the benzene ring. Excursions of sulfur atoms from the plane of the benzene ring do not exceed 0.005 nm.

Phenol-2,6-disulfo Acid + Poly(vinyl Alcohol)

As it was known [3] that the insertion of PSA into the polymer matrix of PVA or similar polymers leads to an increase in the thermal stability of complexes with water and facilitates an increase in parameters of the proton transport, the next stage of work consisted of the simulation of interactions between the initial compo-

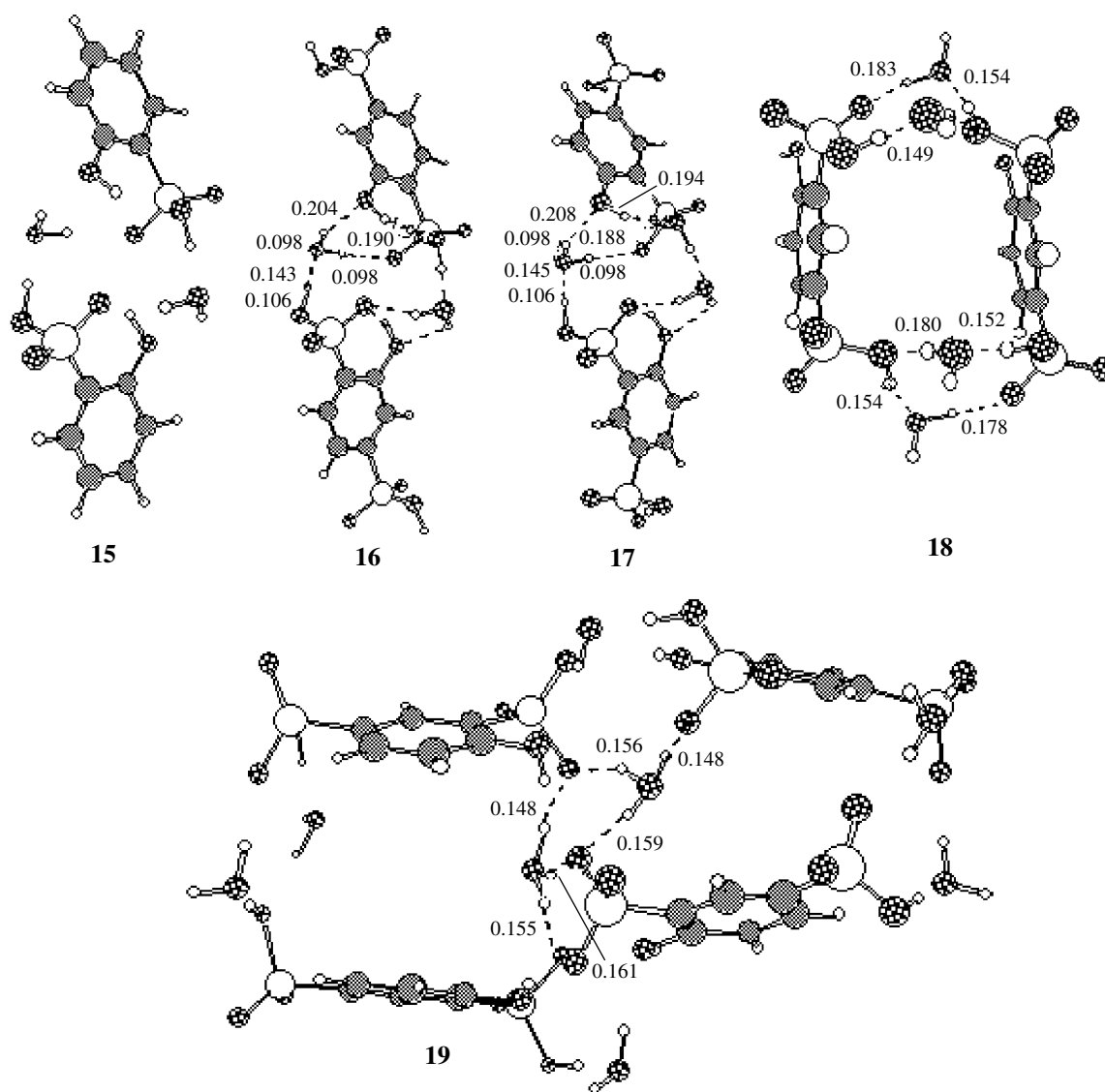


Fig. 4. Scheme illustrating the formation of dimers and tetramer out of various phenoldisulfonic acids and water molecules. Numbers in the figure mark the most substantial distances between atoms (expressed in units of nm).

nents and the paths for the proton transport in these systems.

Figure 5 shows various isomers of a fragment of a PVA chain (isomers **20–22**). As can be inferred from the calculation, all the carbon atoms in a PVA molecule lie in one plane. Isomer **20**, in which all the OH groups lay in one plane (O–O = 0.274 nm, O–H = 0.19 nm), is most stable; the rotation of an OH group by 120° leads to an energy increase by 15 kJ mol⁻¹—isomer **21**; the rotation of another OH group—to an energy increase by another 17.1 kJ mol⁻¹—isomer **22** (Fig. 5).

The interaction of phenoldisulfonic acids with PVA yields a water molecule and may lead to the formation of oligomer complexes **23** and **24** (p-2,6-dsa with PVA), **25** (p-2,5-dsa with PVA), and **26** (p-2,4-dsa with PVA)

(Fig. 5). Isomer **23** is situated in the energy scale by 1.7 kJ mol⁻¹ lower than isomer **24**. Isomer **23** differs from isomer **24** by the rotation of the phenol OH group and by the presence of a hydrogen bond between an OH fragment and an oxygen atom. It should be noted that isomer **24** is situated in the energy scale by 4.2 and 10.9 kJ mol⁻¹ lower than structures **25** and **26** that are formed from PVA and, respectively, p-2,5-dsa and p-2,4-dsa.

Consider the process of interaction of PVA with most stable isomer p-2,6-dsa. As follows from the table, the reaction of the formation of structure **24** out of isomer PVA (**20**) (Fig. 5) and p-2,6-dsa (**11**) (Fig. 3), which yields a water molecule, is endothermic by 19.2 kJ mol⁻¹ (table, scheme 11). The implication is

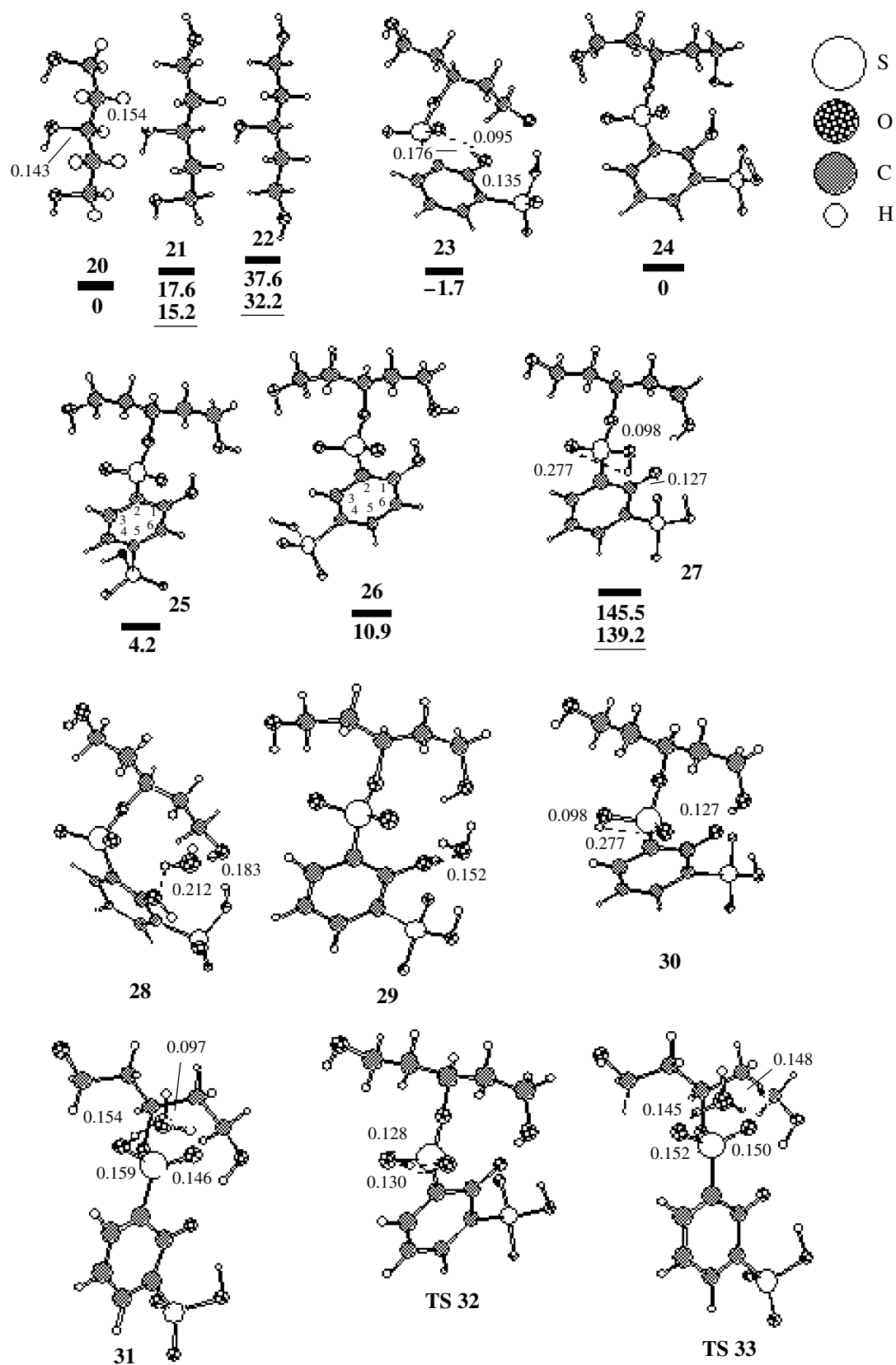


Fig. 5. Scheme illustrating the formation of structures in the system PVA-PSA. Numbers in the figure mark the most substantial distances between atoms (expressed in units of nm) and relative energies of isomers (in kJ mol^{-1}) calculated with allowance (underlined values) and without allowance (not underlined values) made for the energy of zero vibrations (ZPE).

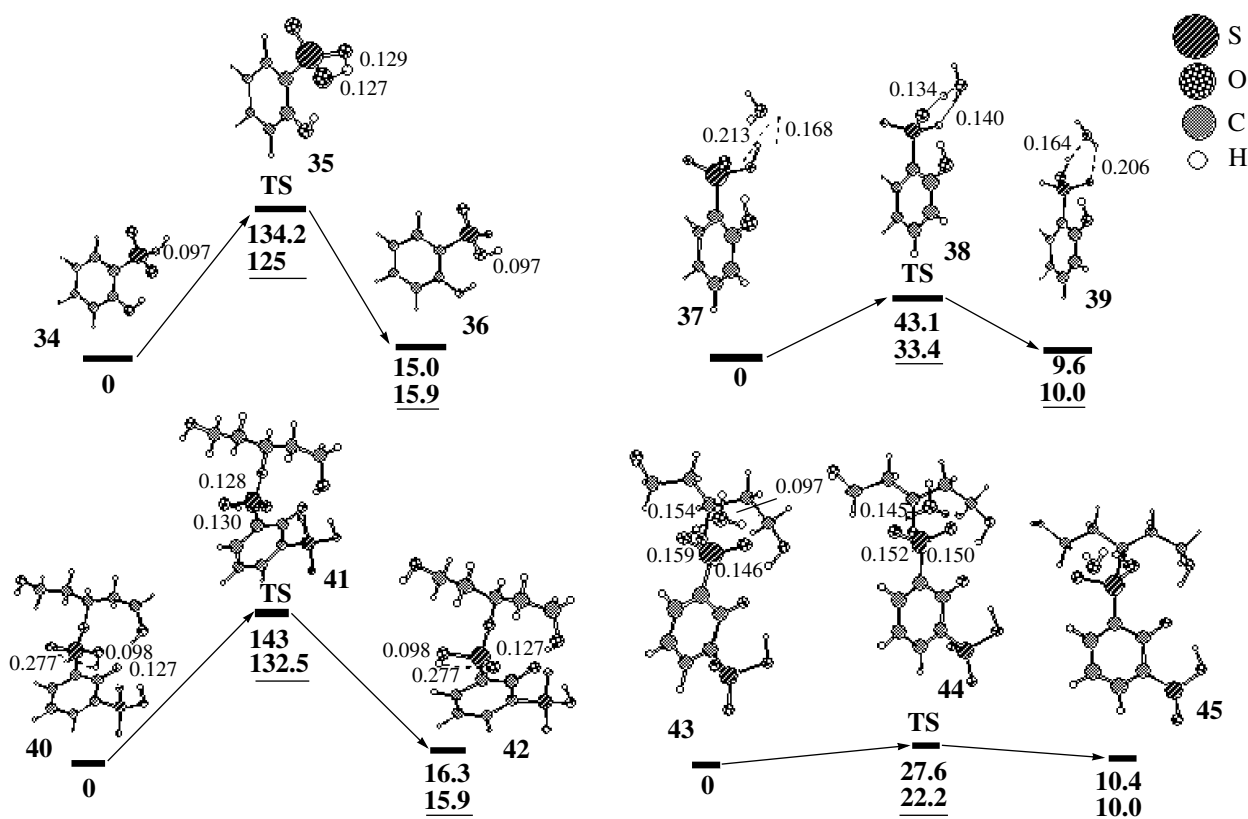


Fig. 6. Scheme of the path of immediate migration of the proton as calculated for *o*-PSA and *p*-2,6-dsa. Numbers in the figure mark the most substantial distances between atoms (expressed in units of nm) and relative energies of isomers (in kJ mol^{-1}) calculated with allowance (underlined values) and without allowance (not underlined values) made for the energy of zero vibrations (ZPE).

that the release of a water molecule during the formation of such a structure is energetically unfavorable. As shown below, under these conditions the water molecule must stay near the *p*-2,6-dsa fragment and be bonded to it by hydrogen bonds.

Isomer **27**, in which the hydrogen atom passes from the OH group to the SO_3 group, is situated in the energy scale by $139.2 \text{ kJ mol}^{-1}$ higher than isomer **24**. The C–O bond in isomer **27** is shorter by 0.009 nm than the C–O bond in isomer **23** and the S–OH bond in isomer **27** is longer by 0.014 nm than the corresponding S–O bond in isomer **23** (Fig. 5).

Let us find out what happens when a water molecule stays near the *p*-2,6-dsa fragment in the course of interaction between *p*-2,6-dsa and PVA. If a water molecule is coordinated by an oxygen atom to the hydrogen atom of an OH group of PVA, the reaction of interaction of PVA (isomer **20**) (Fig. 5) with *p*-2,6-dsa (isomer **11**) (Fig. 3) with the formation of structure **28** (Fig. 5) is exothermic by 49.7 kJ mol^{-1} (table, scheme 12), whereas the reaction of interaction of PVA (isomer **20**) (Fig. 5) with *p*-2,6-dsa (isomer **11**) (Fig. 3) with the formation of structure **29** (Fig. 5) is exothermic by 49.7 and 61.4 kJ mol^{-1} for a calculation with allowance and

without allowance for the energy of zero vibrations (ZPE), respectively (table, scheme 13). The reaction of the attachment of a water molecule to the SO_3H group in structure **30** with the formation of structure **31** is exothermic by 69.8 and 79.8 kJ mol^{-1} with allowance and without allowance for the energy of zero vibrations, respectively (table; scheme 14).

The results of calculations show that it is quite difficult to tear a water molecule off isomers **28**, **29**, and **31** (Fig. 5). The energy required for the tearing-off may be estimated as $46\text{--}79 \text{ kJ mol}^{-1}$. This is, probably, an explanation for the fact that even a prolonged evacuation of specimens (for more than a week) does not lead to a full loss of water. The residual content of water in all films after evacuation amounts to $1.0 \pm 0.2 \text{ mol}$ of water per mole of a sulfonic acid.

The proton migration was studied by investigating *p*-2-sa and *p*-2,6-dsa. In Fig. 6 we show a path of immediate migration of a proton from one oxygen atom of the SO_3 group to another: from isomer **34** to isomer **36** through transition state TS (**35**). The inference is that an immediate migration of the proton would require overcoming a barrier of a magnitude 125 kJ mol^{-1} for the direct and $109.1 \text{ kJ mol}^{-1}$ for the reverse reaction.

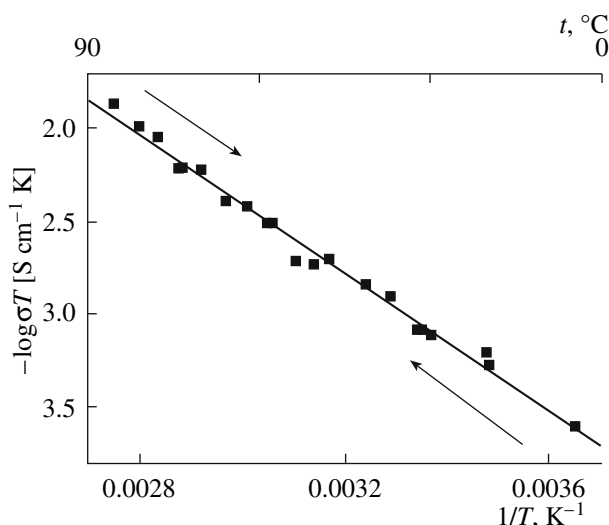


Fig. 7. The temperature dependence of conductivity of p-2,4-dsa in the temperature interval extending from zero to 90°C in a vacuum.

A barrier as large in magnitude (143 kJ mol⁻¹ for the direct and 130.8 kJ mol⁻¹ for the reverse reaction, Fig. 6) happens in the case of the passing of a proton in the model system from isomer **40** to isomer **42** through a barrier corresponding to transition state TS (**41**). Thus, a calculation implies that, in anhydrous environment, the proton migration in PSA via a channel of immediate transfer is hindered by a high activation barrier of 125–132 kJ mol⁻¹.

The process of the proton transport along the same SO₃H group in the presence of water is illustrated by the example of passing from isomer **37** to isomer **39** through a barrier corresponding to transition state TS (**38**) (Fig. 6). As seen from Fig. 6, in this case, the proton transport is realized by means of a relay mechanism. In transition state **38**, two hydrogen atoms of the H₃O⁺ group are bound to the oxygens of the SO₃ group (distance O–H is equal to 0.134–0.140 nm, distance O–O is equal to 0.241–0.242 nm). In the process of the relay mechanism, the proton from one of the oxygens of the SO₃ group passes to the water molecule coordinated to this particular group and, simultaneously, the water molecule transfers one of its protons to the second oxygen atom of the SO₃ group. The energy of the activation barrier in the presence of water is equal to 33.4 kJ mol⁻¹ for the direct and 23.4 kJ mol⁻¹ for the reverse reaction. This value is smaller than in anhydrous environment by 92 kJ mol⁻¹.

A qualitatively similar effect happens in the model system in the case of a similar transfer of a proton from isomer **43** through barrier TS (**44**). The water molecule in isomer **45** is coordinated by the oxygen atom to the proton of the SO₃H group (distance O–H is equal to

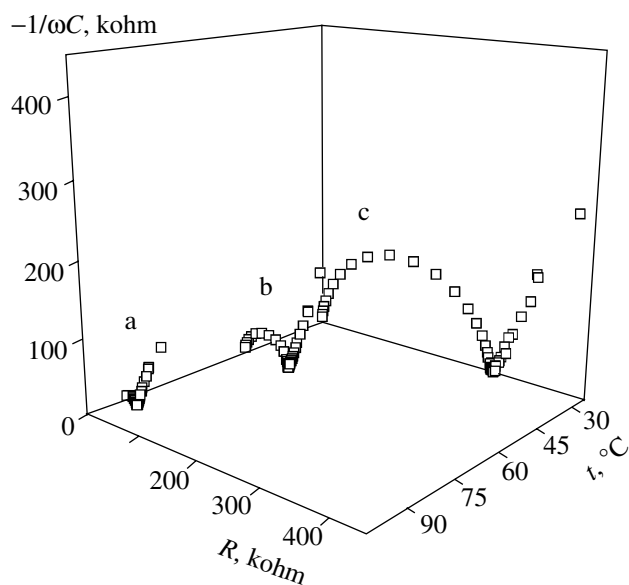


Fig. 8. Transformation of impedance spectra for dihydrate p-2,4-dsa in a three-dimensional representation for temperatures equal to (a) 91, (b) 53, and (c) 24°C.

0.154 nm) (Fig. 5). In the presence of water, the process of the proton transport onto the same SO₃H group is connected with the overcoming of barrier TS (**44**) (Fig. 6), in which two hydrogen atoms of the H₃O⁺ group are bound to the oxygens of the SO₃ group (distance O–H is equal to 0.145–0.148 nm, distance O–O is equal to 0.245 nm). In the presence of water, the energy of the activation barrier is equal to 22.2 kJ mol⁻¹. This value is smaller than in anhydrous environment by 108.7 kJ mol⁻¹.

Thus, calculations show that, in the presence of water, proton conductivity is of a relay character, in contradistinction to the proton transport in anhydrous environment. The calculated values of the activation barriers 21–33 kJ mol⁻¹ are close to values measured in the PVA–p-2,4-dsa system in the interval of humidities RH = 15–55 rel % and are equal to 17–25 kJ mol⁻¹ [3].

PROTON CONDUCTIVITY

The method of impedance spectroscopy was used to perform measurements of conductivity in p-2,4-dsa and in specimens of the PVA–p-2,4-dsa system. It was demonstrated that the proton conductivity of dihydrate p-2,4-dsa was equal to 2.5×10^{-6} S cm⁻¹ at a temperature of 25°C (vacuum). The temperature dependence of conductivity is presented in Fig. 7. The activation energy for conductivity was determined with equation (1). It amounts to the value 0.23 eV, which is characteristic of typical proton conductors:

$$\sigma T = \sigma_0 \exp(-E_a/kT), \quad (1)$$

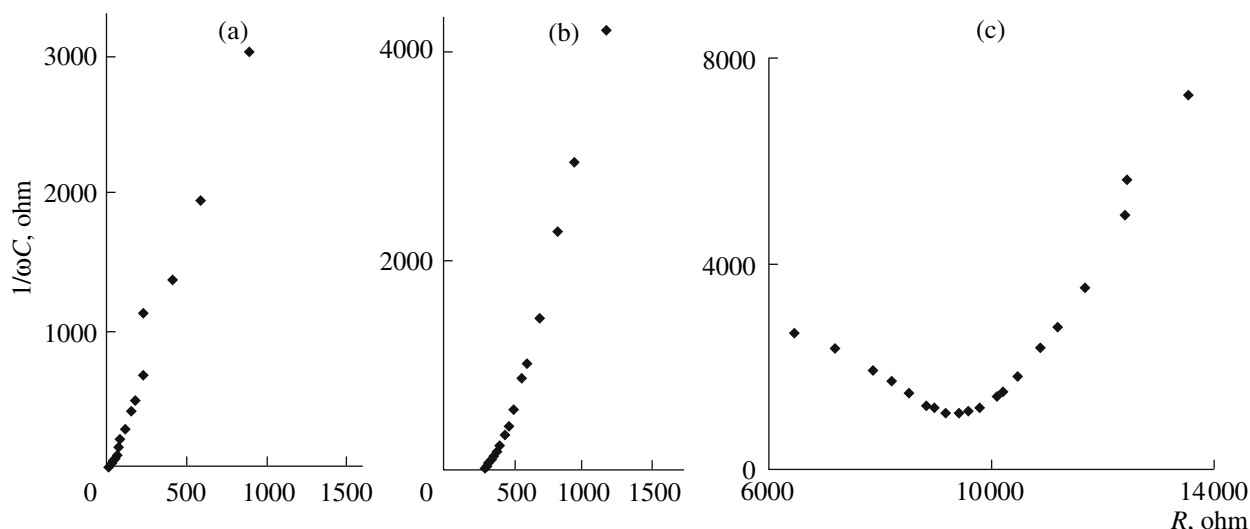


Fig. 9. Impedance spectra for films of different composition at RH = 32 rel % with the molar ratio [PVA] : [p-2,4-dsa] equal to (a) 4 : 1, (b) 8 : 1, and (c) 20 : 1.

where σ is a conductivity, $S\text{ cm}^{-1}$; T is a temperature, K; σ_0 is a factor, $S\text{ cm}^{-1}\text{ K}$; E_a is an activation energy, eV; and k is Boltzmann's constant, eV K^{-1} .

Impedance spectra for cells at different temperatures combine a semicircle and a segment of a straight line situated at an angle of 45° (Fig. 8). The electrolyte resistance R_e was determined as the right-hand cut-off of the intersection of the semicircle with the axis of real resistances. Upon increasing the humidity from 0 to 15 rel % and the temperature of surrounding environment to 90°C , the conductivity increases from 10^{-6} to 10^{-5} S cm^{-1} ; at a humidity of 19 rel % compound starts to deliquesce and converts into tetrahydrate p-2,4-dsa [10].

In the system based on PVA and p-2,4-dsa there was discovered a high conductivity of polymer electrolytes.

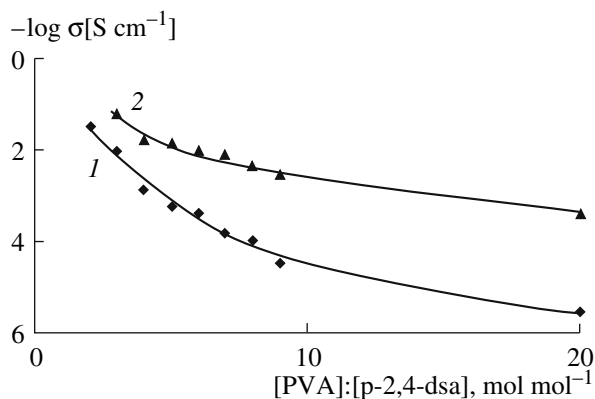


Fig. 10. Dependences of conductivity of films of different composition on composition at different humidities as follows: (1) 32 and (2) 44 rel %, 25°C .

We investigated the dependence of conductivity in such systems on the concentration of the inserted sulfonic acid, on the temperature and humidity of the environment. In Fig. 9 we present impedance spectra for films of different composition at RH = 32 rel % and in Fig. 10—the dependence of the conductivity of the films of different composition on humidity. The impedance spectra are either a straight line (in that case R_e is the left-hand cut-off of the intersection of the straight line with the axis of real resistances) or a segment of a semicircle with a segment of a straight line situated at an angle of 45° (in that case R_e —the right-hand cut-off of the intersection of the segment of the semicircle with the axis of real resistances). At a humidity of less than 20 rel %, the proton conductivity decreases to

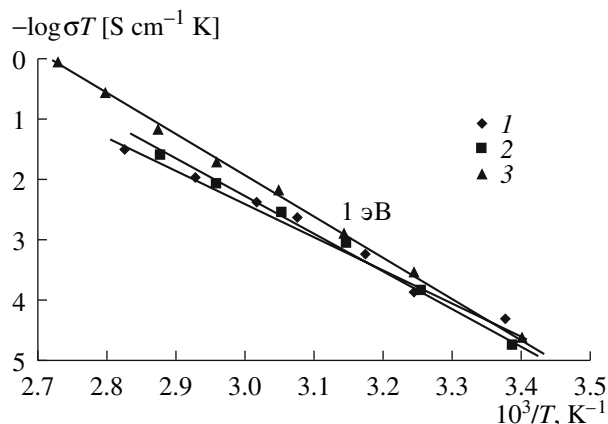


Fig. 11. The temperature dependences of conductivity in the PVA-p-2,4-dsa system in the temperature interval extending from zero to 90°C , in a vacuum. Molar ratio [PVA] : [p-2,4-dsa] is equal to (1) 20 : 1, (2) 10 : 1, and (3) 6 : 1.

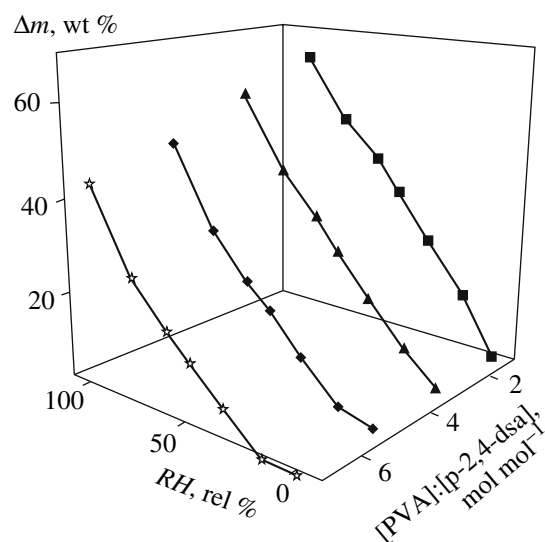


Fig. 12. The increase in the film weight Δm following the absorption of water.

$10^{-7} \text{ S cm}^{-1}$ at room temperature, in so doing, the activation energy for conductivity increases to 1 eV, which testifies to a change in the relay mechanism of the proton transport to a hopping mechanism. In Fig. 11 we present the temperature dependence of the conductivity in polymer electrolytes of different composition in the system PVA–p-2,4-dsa that were kept for a long time in a dry box with argon. The decrease in the conductivity in the system with the lowering of the humidity of the surrounding environment is connected with the lowering of the content of water in the polymer electrolyte, i.e. with the lowering of the degree of hydration (Fig. 12). It was demonstrated that films of the composition PVA–p-2,4-dsa in a 4 : 1 molar ratio in the pres-

ence of satisfactory mechanical properties possess, at a humidity in the interval extending from 32 to 95 rel %, a record-breaking proton conductivity of 10^{-5} to $10^{-2} \text{ S cm}^{-1}$ with the activation energy for conductivity equal to 0.2–0.4 eV.

The obtained experimental data concerning parameters characterizing the proton transport in crystalline dihydrate p-2,4-dsa and polymer electrolytes based on PVA and p-2,4-dsa well agree with the data of a quantum-chemical simulation.

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