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Solvation Effects in Hydrolysis of 2-Methylbenzenesulfonyl Halides in Binary Solvents H_2O–*i*-PrOH, H_2O–*t*-BuOH, and H_2O–1,4-Dioxane with Low Concentration of Organic Component

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Abstract — Activation parameters of hydrolysis of 2-methylbenzenesulfonyl chloride are studied, as influenced by the mole fraction of an alcohol in binary solvents H_2O–*i*-PrOH and H_2O–*t*-BuOH. The dependences of the activation parameters on the mole fraction of the second component (X_2) are strongly nonmonotonic, like those for the previously studied hydrolysis of toluenesulfonyl chloride and bromide in aqueous dioxane. The position of the extrema along the composition axis is controlled by the hydrophobicity of nonelectrolytes. Sharp minima of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in the binary system H_2O–*i*-PrOH at X_2 0.03 are caused by specific solvation of the sulfonyl chloride.

Being added even in trace amounts ($X_2 < 0.001$) to water, a nonaqueous component induces reorganization of the local structure of the solution, expanding then throughout the hydrogen bond network [1–4]. Such a stabilization of the solvent structure causes solvation effects reflected in nonmonotonic concentration dependences of physical and thermodynamic properties of the binary system [3, 4]. Hydrolysis of a third component (hydrophobic aromatic polyfunctional substrate) in a binary aqueous organic solvent is characterized by nonmonotonic concentration dependences of the kinetic parameters [5]. The rate constants and activation parameters of water- [6, 7] or base-catalyzed [8–10] hydrolysis of esters and halides of arenecarboxylic acids demonstrate strongly nonmonotonic dependences on the reaction mixture composition. Since molecules of such substrates are heterofunctional and poorly soluble in water and in dilute aqueous nonelectrolyte solutions [1, 3, 5], solvation effects in processes involving bioactive compounds could be judged from the kinetic parameters of their hydrolysis [1, 2, 5, 11, 12].

The activation parameters of hydrolysis of methyl-substituted benzenesulfonyl halides [13], especially, of *o*-methyl-substituted derivatives [14–16] were found to be highly sensitive to the solution composition. In these compounds, the hydrophobic *o*-methyl group controls the orientation of the sulfonyl halide center in nucleophilic attack by water molecules [16], causing specific conditions of hydration of this center. The activation parameters of hydrolysis of 2-methylbenzenesulfonyl halides change strongly nonmonotonically on adding dioxane to water over the X_2 range 0–0.14, demonstrating two minima of the activation enthalpy (and, correspondingly, activation entropy) at X_2 0.01–0.05 and 0.12 [14–16].

In this work we studied the effect of the nonaqueous component of the binary solvents H_2O–*i*-PrOH and H_2O–*t*-BuOH on the activation parameters of hydrolysis of 2-methylbenzenesulfonyl chloride (**I**) in water-rich systems.

Table 1 shows the hydrolysis rate constants of **I** in the system H_2O–*i*-PrOH (X_2 0.0395) at seven temperatures. From the temperature dependences we determined the quasithermodynamic activation parameters of hydrolysis of **I** in the binary systems H_2O–*i*-PrOH (22 compositions) and H_2O–*t*-BuOH (11 compositions). The results are presented in Tables 2 and 3 and Fig. 1). From the activation parameters we estimated the effective pseudo-first-order rate constants at 298 K (k_{298}, Tables 2 and 3). For each composition of the binary mixtures we calculated the contributions ϑ (%) of $|T\Delta S^{\neq}|$ to $\Delta G^{\neq}$ (Tables 2 and 3, Fig. 2). For comparison, in Fig. 2 we present also the dependences of ϑ on X_2 for hydrolysis of **I** and 2-methylbenzenesulfonyl bromide (**II**) in H_2O– dioxane mixtures.

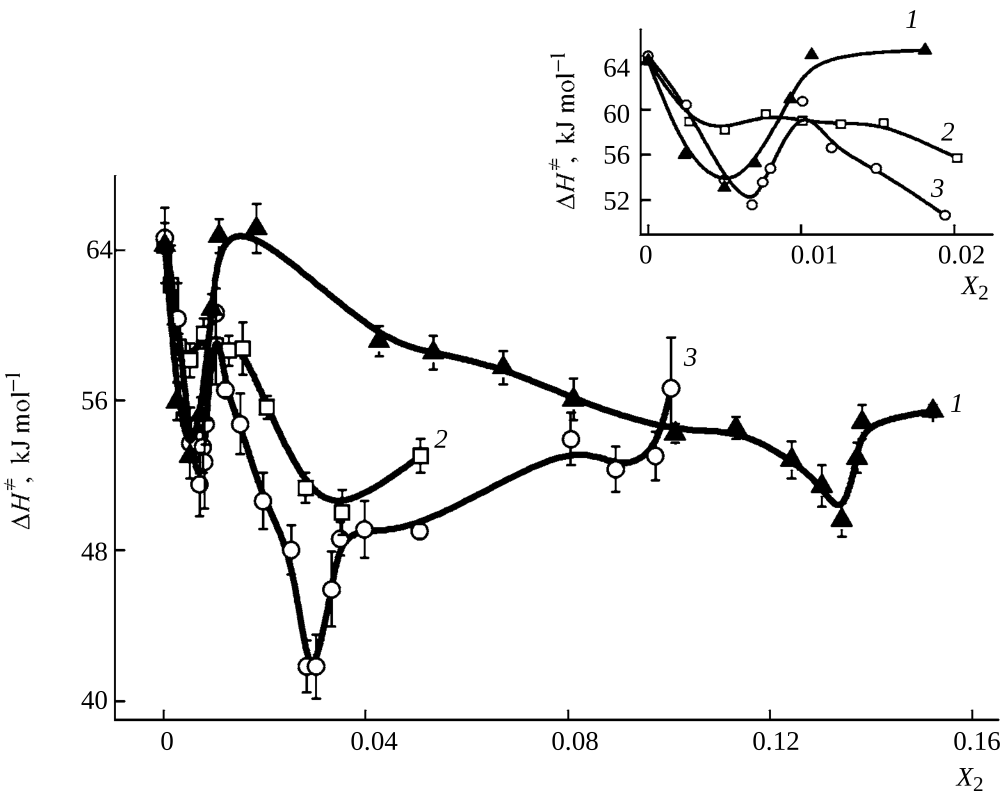


Fig. 1. Activation enthalpy of hydrolysis of **I** as a function of the mole fraction of a nonaqueous component (X_2): (*1*) dioxane, (*2*) *t*-BuOH, and (*3*) *i*-PrOH. The insert shows the initial section on a larger scale.

The dependences of $\Delta H^{\neq}$ and ϑ on X_2 for the sulfonyl halides studied are strongly nonmonotonic (Figs. 1 and 2), the first minimum of $\Delta H^{\neq}$ (correspondingly, the first maximum of ϑ) being found at X_2 0.005–0.007, regardless of the nature of a nonaqueous component. The subsequent trends in ϑ and $\Delta H^{\neq}$ are strongly specific for each of the systems. The results obtained can be interpreted in terms of the concept we proposed in the previous works [14–17].

Table 1. Effective rate constants of hydrolysis of 2-methylbenzenesulfonyl chloride in the system H_2O–*i*-PrOH (mole fraction of *i*-PrOH 0.0395)

T, °C	$(k \pm \Delta k) \times 10^3$, s^{-1}	*r*	$t_{exp}/t_{0.5}$ [a]
22.75	2.58 ± 0.01	0.9999	4.8
26.78	3.20 ± 0.01	0.9999	3.8
32.24	5.25 ± 0.04	0.9997	5.3
34.66	5.75 ± 0.02	0.9999	5.3
39.17	8.10 ± 0.05	0.9998	4.4
46.04	11.40 ± 0.05	0.9999	4.8
52.60	17.7 ± 0.2	0.9998	4.8

[a] ($t_{exp}/t_{0.5}$) Duration of the experiment expressed in the half-conversion times.

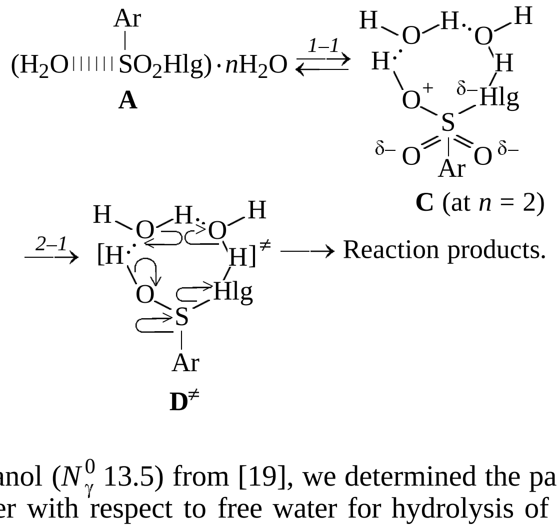
The rate of hydrolysis of sulfonyl halides **I** and **II** strongly depends on the water concentration. The partial order of the reaction with respect to water in the water–dioxane solvent was estimated to be close to 3 (taking no account of the limiting hydration number of dioxane) [15, 18], and the process is characterized by low activation entropy (–70– to –120 J mol^{-1} K^{-1}). Along with the results of quantum chemical calculations for hydrolysis of benzenesulfonyl chloride in water clusters [17], these facts are consistent with the mechanism of catalyzed nucleophilic substitution at the sulfonyl reactive center with cooperative participation of (n + 1) water molecules in formation of cyclic transition states (n is the number of water molecules catalyzing hydrolysis) [15, 16]. In the scheme below we show the mechanism of hydrolysis of aromatic sulfonyl halides for the case of n = 2 (designations in the scheme correspond to those in [15, 16]; the transition state **B** of the reversible stage *1–1* is not presented).

From our experimental results, using the limiting hydration numbers of isopropanol (N_{γ}^{0} 7) and *tert*-

Table 2. Activation parameters and interpolated k_{298} values for hydrolysis of **I** in the system H_2O–*i*-PrOH

X_2[a]	$\Delta H^{\neq}$, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}	$(k_{298} \pm \Delta k) \times 10^3$, s^{-1}	r[b]	n[c]	ΔT[d]	ϑ[a]
0.0	64.7±0.8	74.6±2.7	3.59±0.16[f]	0.9995	6	34.7	25.5
0.0025	60.4±1.9	88.0±6.2	4.07±0.40	0.9981	6	26.7	30.3
0.0050	53.8±1.9	109.3±6.0	4.55±0.57	0.9982	5	25.0	37.7
0.0068	51.6±1.7	117.4±5.6	4.23±0.45	0.9931	6	30.9	40.4
0.0075	53.6±1.4	110.5±4.5	4.30±0.29	0.9964	7	26.3	38.0
0.0078	52.8±2.5	113.6±8.1	4.14±0.59	0.9922	6	29.9	39.1
0.0080	54.8±2.1	107.2±6.7	4.00±0.44	0.9969	5	22.3	36.9
0.0101	60.7±1.3	88.3±4.3	3.59±0.26	0.9997	6	26.8	30.2
0.0120	56.6±0.4	99.6±1.3	4.81±0.14	0.9998	5	31.0	34.4
0.0149	54.8±2.6	107.0±8.3	4.03±0.73	0.9974	5	29.2	36.8
0.0194	50.7±1.5	120.5±4.8	4.20±0.45	0.9994	5	30.9	41.5
0.0250	48.1±1.3	129.1±4.2	4.12±0.24	0.9973	7	27.3	44.5
0.0280	41.9±1.4	150.6±4.3	3.90±0.32	0.9961	7	32.3	51.7
0.0299	41.9±1.7	151.0±5.4	3.67±0.36	0.9960	6	30.4	51.8
0.0330	46.0±2.0	137.5±6.3	3.54±0.40	0.9952	6	30.9	47.1
0.0347	48.7±0.9	128.3±2.9	3.64±0.17	0.9982	7	33.3	44.0
0.0395	49.2±1.5	128.1±4.9	3.01±0.22	0.9984	7	25.8	43.7
0.0504	49.1±0.4	129.0±1.2	2.84±0.06	0.9998	6	23.8	43.9
0.0803	54.0±1.4	120.5±4.1	1.08±0.09	0.9972	7	29.4	39.9
0.0892	52.5±1.2	134.2±3.4	0.92±0.06	0.9956	6	28.4	42.3
0.0971	53.1±1.4	128.0±3.9	0.64±0.04	0.9995	6	27.8	41.8
0.1002	56.7±2.7	116.9±8.4	0.56±0.11	0.9929	6	23.4	38.1

[a] Mole fraction of *i*-PrOH, [b] correlation coefficient of the Arrhenius curve, [c] number of the experimental rate constants included in the temperature dependence, [d] Experimental temperature interval, [e] $\vartheta = (-0.298\Delta S^{\neq})100/\Delta G^{\neq}$, %, and [f] 3.82±0.37 [15].



butanol (N_γ^0 13.5) from [19], we determined the partial order with respect to free water for hydrolysis of **I** in the systems H_2O–*i*-PrOH and H_2O–*t*-BuOH. The resulting values (1.83±0.07 and 1.8±0.2, respectively) are close to 2 (Fig. 3). Note that the free water concentration was estimated as $c_1^* = c_1 - N_\gamma^0 c_2$, where c_1 and c_2 are the stoichiometric concentrations of water and alcohol, respectively, and N_γ^0 is the limiting hydration number of the alcohol [19]. Evidently, elimination of the chloride ion proceeds through formation of an eight-membered complex **C** with two more water molecules in addition to the water molecule as a nucleophilic agent.

Previously we have theoretically demonstrated [17] that any stabilization of the solvent structure results

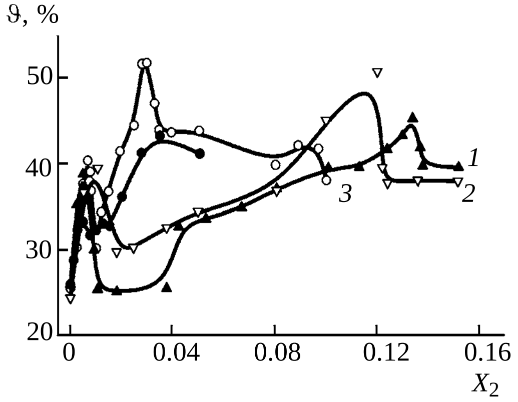


Fig. 2. ϑ as a function of the mole fraction of a nonaqueous component in hydrolysis of **I** in (*1*) H_2O–dioxane, (*3*) H_2O–*i*-PrOH, and (*4*) H_2O–*t*-BuOH, and (*2*) of **II** in H_2O–dioxane.

Table 3. Activation parameters and interpolated k_{298} values for hydrolysis of **I** in the system H_2O–*t*-BuOH

X_2[a]	$\Delta H^{\neq}$, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}	$(k_{298} \pm \Delta k) \times 10^3$, s^{-1}	r	n	ΔT, deg	ϑ
0.0012	62.2 ± 2.1	84.2 ± 6.9	3.20 ± 0.33	0.9947	6	35.2	28.8
0.0027	58.9 ± 0.7	94.3 ± 2.4	3.55 ± 0.13	0.9998	7	28.8	32.3
0.0050	58.2 ± 0.9	97.1 ± 2.8	3.44 ± 0.13	0.9996	6	27.7	33.3
0.0077	59.6 ± 0.8	92.8 ± 2.5	3.27 ± 0.11	0.9997	9	32.7	31.7
0.0101	59.0 ± 2.1	94.6 ± 6.9	3.31 ± 0.32	0.9973	8	32.9	32.3
0.0126	58.7 ± 0.8	97.5 ± 2.6	2.57 ± 0.11	0.9996	6	27.9	33.1
0.0154	58.8 ± 1.4	96.4 ± 4.6	2.87 ± 0.22	0.9995	6	27.6	32.8
0.0202	55.7 ± 0.6	106 ± 2	3.16 ± 0.13	0.9996	5	33.0	36.2
0.0278	51.4 ± 0.8	121 ± 3	2.91 ± 0.13	0.9996	7	32.0	41.3
0.0351	50.1 ± 1.2	128 ± 4	2.22 ± 0.13	0.9994	6	31.8	43.3
0.0506	53.1 ± 0.9	125 ± 3	0.961 ± 0.081	0.9991	8	29.9	41.2

[a] Mole fraction of *t*-BuOH; see Table 2 for the other designations.

in strengthening of the H bonds in intermediate **C** (see scheme), which should decrease the activation parameters of its breakdown into reaction products and, therefore, the effective activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of hydrolysis. Decrease in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is equivalent to increase in ϑ. Figures 1 and 2 show that, in all cases, ϑ tends to increase with increasing X_2. Correspondingly, $\Delta H^{\neq}$ tends to decrease. This trend is consistent with the tendency to stabilization of the water structure in water-rich binary solvents with increasing concentration of the nonaqueous component to X_2 0.12, 0.09, and 0.05 for dioxane, *i*-PrOH, and *t*-BuOH, respectively [3, 4, 10, 20–23]. Following the common views [3, 21–24], stabilization of the water structure through strengthening of the H bonds is caused by some constraints on the translational and rotational mobility of water molecules as a result of partial filling of the cavities of the structure with nonelectrolyte molecules. The maximal stabilization corresponds to the composition at which all the cavities are filled, and the maximum of the heat of mixing of water with the alcohol is realized [23]. At this composition, the enthalpy of solution of the hydrolyzed substrate is maximally endothermic, and the activation enthalpy of hydrolysis is the minimal [24].

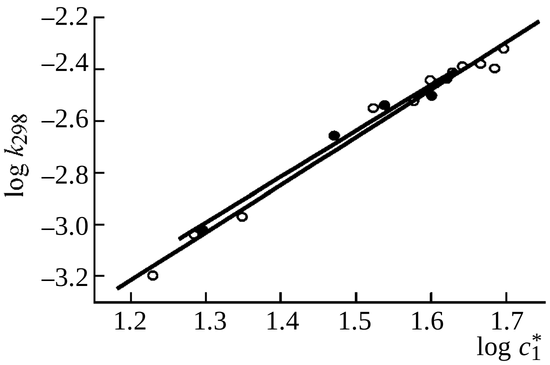


Fig. 3. Hydrolysis rate constant of **I** as a function of the free water concentration c_1^* in (*1*) H_2O–*i*-PrOH and (*2*) H_2O–*t*-BuOH.

At X_2 0.1–0.15, according to Arnett *et al.* [23], the partial molar enthalpies of solution of a series of substrates (*t*-BuCl, *i*-PrBr, and EtOAc) in aqueous ethanol pass through maxima. For the aromatic substrates $PhCH_2Cl$ and $PhOSO_2Me$ poorly soluble in dilute aqueous ethanol, they only observed descending branches near X_2 0.1 with increasing nonelectrolyte concentration, suggesting the presence of maxima of the enthalpy of solution. Since the maxima of the enthalpy of solution of the most of the substrates studied [23] corresponded to the minima of the activation enthalpy of their hydrolysis, one may expect that this is also the case for the aromatic sulfonyl halides. In hydrolysis of compounds **I** and **II** similar in their nature to $PhOSO_2Me$, the weakly pronounced maxima of the activation enthalpy (ϑ maxima) at X_2 0.04, 0.09, and 0.13 for *t*-BuOH, *i*-PrOH, and dioxane, respectively (Fig. 1), should correspond to the maximal stabilization of the solvent structure. The observed relative similarity of the ϑ and $\Delta H^{\neq}$ values in different solvents at the indicated concentrations suggests the same origin of these extrema associated with reaching the maximal stabilization of the solvent structure at the "critical concentration of hydrophobic interaction" [7]. Below this factor will be discussed in more detail. All these findings are consistent with the known trend [23, 24] that, with increasing size and hydrophobicity of a nonelectrolyte molecule, the solvent structure becomes stabilized at lower X_2. For example, the X_2 corresponding to the minima of the activation enthalpy of hydrolysis of *t*-BuCl in dilute aqueous alcohols depends on the number of alkyl groups in an alcohol molecule, increasing in the order *t*-BuOH < *i*-PrOH < EtOH [24]. Similar conclusion was made in [25] on the basis of a correlation obtained between the enthalpy of transfer of a nonaqueous component and the mole fraction N of hydrophobic groups of alcohols (up to N 0.17). Therefore, our results can be regarded as one more evidence in favor of the fact that nonelectrolyte molecules stabilize the structure of aqueous organic mixtures, which was demonstrated in recent works [26–30]. In this context, some doubts cast upon even local structurization of water in the presence of nonelectrolytes [12, 31] appear to be not quite substantiated.

The increase in ϑ with increasing X_2 suggests that, in our case, hydrolysis is an entropy-controlled process, since the activation enthalpy changes in the opposite direction to $\Delta G^{\neq}$ [9, 10]. However, contrary to the general trend, at certain concentrations of a nonaqueous component, ϑ starts to decrease with increasing X_2. In all the binary solvents studied, in the ϑ–X_2 curves obtained for hydrolysis of **I**, the X_2 range where ϑ especially strongly declines is 0.005–0.01. In the case of hydrolysis of **II**, this range is shifted toward somewhat higher dioxane concentrations (X_2 0.01–0.02). Such a strong decrease in ϑ on the background of undoubtedly increasing structurization of water, in our opinion [14, 15], is caused by an increased probability of realization in the indicated range of such V-configurations in which formation of stable clathrate [2, 3, 17, 32] or, in other terms, quasicrystalline shells [22] around molecules of certain substrates becomes energetically more profitable as compared to their specific hydration. By virtue of water "freezing" in such a clathrate shell, the enthalpy and entropy of the initial state considerably decrease [3–5], resulting in increase in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ and decrease in ϑ. In these "solvation wells" (quasiclathrate shells [14–16]), the state of sulfonyl halide molecules without specific hydration shells is close to the state of a guest in the structure of a true clathrate. The probability of formation of such wells is controlled by the nonelectrolyte nature and concentration, and that of getting into them, in accordance with the principle of complementarity [27], by the size and geometry of the sulfonyl halide molecule. The positions of the minima of ϑ and, correspondingly, maxima of $\Delta H^{\neq}$ along the composition axis are located in the order of decreasing relative hydrophobicity of the nonelectrolytes, i.e., capability of forming clathrates [1]: *t*-BuOH (X_2 0.008), *i*-PrOH (X_2 0.01), and dioxane (X_2 0.038). In this case, the differences between ϑ_{max} (in straight water) and ϑ_{min} (Fig. 2) correlate well with the second virial coefficients B_{22} (cm^3 mol^{-1}) at 298 K [2][1] (increase in B_{22} suggests decrease in the relative hydrophobicity of the corresponding components and in their effect on the structure of water). Therefore, the lower (ϑ_{max} – ϑ_{min}), the more structured is water in a solvent and the lower is the probability of realization of V-structures in water that would be complementary in size to sulfonyl halide molecules, and, finally, the shorter the intervals between the extrema along the composition axis.

The activation parameters are influenced also by substrate–nonaqueous component interaction, which are realized throughout the X_2 range from 0 to the critical concentration of hydrophobic interaction [7], i.e., until completion of stabilization of the solution structure, after which molecules of the nonaqueous component start to associate into clusters. After reaching the critical concentration, ϑ rapidly decreases ($\Delta H^{\neq}$ rapidly increases), which, in our opinion, is caused by decrease in the standard enthalpies and entropies of the initial states of the substrates as a result of inclusion of the sulfonyl halide molecules in the clusters of the nonaqueous component [15, 16]. Decrease in ϑ in the course of hydrolysis of **I** in H_2O–*t*-BuOH, H_2O–*i*-PrOH, and H_2O–dioxane mixtures starting from X_2 0.04, 0.1, and 0.13, respectively [in the case of **II**, starting from X_2 0.12] is initiated by the formation at the indicated concentrations of fluctuating clusters from molecules of the nonaqueous component. This confirms the conclusions made in [5, 7] that the critical concentration of a nonaqueous component decreases as its hydrophobicity increases.

However, some nonelectrolytes taken in certain concentration in a binary aqueous-organic solvent can decrease the activation parameters of hydrolysis of the sulfonyl halide not only by virtue of stabilization of the structure of water in the solvent or through hydrophobic interaction with its molecules, but also by virtue of hydrogen bonding of the sulfonyl halide with the nonaqueous component or its hydration shell. In particular, in the system H_2O–*i*-PrOH, the observed increase in ϑ over the X_2 range from 0.01 to 0.03 is apparently inconsistent with the relative hydrophobicity of isopropanol (Fig. 2). The critical concentration of isopropanol is close to X_2 0.08–0.09 [20–26]. Therefore, the earlier maximum of ϑ at X_2 *i*-PrOH 0.03 is not a result of approaching the critical concentration, but rather a consequence of specific interactions between compound **I** and *i*-PrOH (specifically, between the oxygen atoms of the sulfonyl

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[1] It is more correct to use (dB_{22}/dP) [2], but, unfortunately, reliable data on this parameter are available for dioxane only.

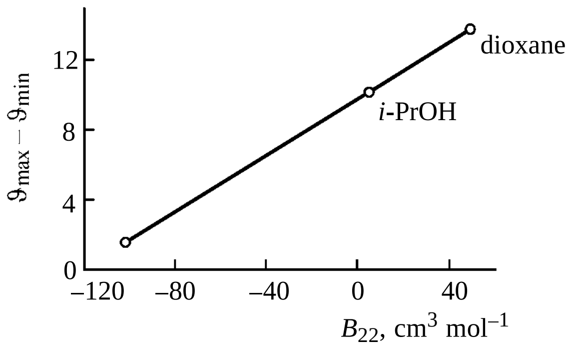

Fig. 4. Difference (ϑ_{max} − ϑ_{min}) as a function of B_{22} for hydrolysis of **I** in binary solvents at 298 K.

group or a water molecule of the cyclic water cluster with the hydroxy group of the alcohol), strengthening the hydrogen bonds in the cyclic intermediate **C** (see scheme). The interaction of molecules of **I** with *i*-PrOH, reaching a maximum at X_2 0.03, resembles the case of specific solvation of an ester with *i*-PrOH molecules in H_2O–*i*-PrOH mixtures [26]. The ϑ value in this system increases with increasing X_2 much more rapidly than in the system with *t*-BuOH as a more hydrophobic nonelectrolyte. The appearance of a maximum of ϑ at X_2 0.03 corresponding to an equally sharp minimum of $\Delta H^{\neq}$ (Fig. 1) suggests that the activation parameters are sensitive to the formation of the intermolecular structures $H_2O\cdots$*i*-PrOH which selectively hydrate the sulfonyl chloride molecule. Near X_2(*i*-PrOH) 0.04, the isotherms of adiabatic compressibility pass through a minimum, reflecting the formation of a clathrate-like structure [33], which is not broken even by adding NaCl to a concentration of 2 mol kg^{-1}. At X_2(*i*-PrOH) 0.04 and 0.13, the volume expansion coefficient is temperature-independent, demonstrating isobestic points of a sort [34]. At the above-indicated concentrations, minima were observed also for the partial molar volumes of the alcohol, interdiffusion coefficients of the solution components, anomalous absorption, acoustic speed variance, and isothermal compressibility [3, 10, 35].

Phenomena similar to those observed in the system H_2O–*i*-PrOH also occur, evidently, in other aqueous binary systems in which nonaqueous components are other lower alcohols and even strong electrolytes, for example, sulfuric acid [36]. Following the views stated in [3], constraint on the translational or rotational mobility of water molecules can originate from both the effect of nonpolar molecules and formation of strong H bonds with solute molecules, i.e., the same effect can be caused by absolutely different mechanisms.

Note finally that the kinetics of hydrolysis in dilute aqueous nonelectrolyte solutions is strongly influenced by the functional groups of the nonelectrolyte, capable of hydrogen bonding and promoting association of the nonelectrolyte with molecules of the hydrolyzable substrate [19].

EXPERIMENTAL

The industrial sample of *o*-toluenesulfonyl chloride was purified according to the procedure described in [15]. The working solutions were prepared gravimetrically from double-distilled water and a nonaqueous component. The kinetics of hydrolysis in aqueous *i*-PrOH was studied spectrophotometrically [13, 14], and in the system H_2O–*t*-BuOH, conductometrically [15]. The hydrolysis rate constants were determined at 6–8 temperatures over at least 25-deg intervals. The quasithermodynamic activation parameters were estimated as in [14, 15]. Isopropanol (analytically pure grade) was purified by the standard procedure [37]. The alcohol was dried for a day over anhydrous potassium sulfate and then distilled with a Vigreux column, taking the fraction 82.3°C (bp 82.4°C [37]). *tert*-Butanol (analytically pure grade) was purified by fractional crystallization [37] and then distilled.

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