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Kinetic Investigation of Hydroxide Ion Attack at High Spin Fe(II) Bromosalicylidine Chelates with Amino Acids in Binary Aqueous Solvents: Initial and Transition State Analysis[1]

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Abstract—We have investigated the kinetics of hydroxide ion attack at iron(II) chelates with 5-bromosalicylidene derivatives of amino acids (alanine, phenylalanine, aspartic acid, histidine, and arginine) in binary aqueous mixed solvents at 298 K. The observed reactivity trends are discussed in connection with the complexes hydrophobicity/hydrophilicity, transfer chemical potentials of hydroxide ion and the complex, and the solvent effects.

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In bioinorganic chemistry, iron(II) complexes with the Schiff's bases serve as useful structural and electronic models of functional sites of heme-containing enzymes. Furthermore, such complexes may be used in asymmetric oxidation of organic substrates, since their structure and catalytic activity are similar to these of iron porphyrins [1]. The complexes of amino acids Schiff's bases act as perfect chelating agents [2, 3] and are highly biologically active [4, 5] and cytotoxic [6]. Additionally, they are regarded as new type of promising antibacterial and anticancer reagents [7].

The solvent effects on reactivity of transition metal complexes have been of interest recently. Most of reactions of inorganic complexes proceed differently in micellar and microemulsion systems as compared with homogeneous solutions. The appropriate use of microemulsions allows for kinetic studies of reactions involving water-insoluble or hydrophobic substrates like the above-described complexes of the amino acids Schiff's bases [8, 9]. The transfer chemical potentials of the inorganic complexes have been investigated in binary aqueous solvents with relation to the reactivity towards substitution and redox processes [10]. A new approach have been corroborated to understand the solvent effects on reactivity, involving analysis of the interaction of the solvent with the initial and the transition reactant states [11]. The solvent effects on the rate constant and activation parameter are generally complex; however, their analysis in terms of the contributions from the initial and transition states can fully explain the trends [8, 9, 12]. Simultaneously, the solvation effects can be probed via changes of the activation volume as function of the solvent properties [13]. The two mentioned approaches are complementary: the analysis of the initial and transition states provides information on solvation changes in the case of reaction involving heterogeneous reactant transfer, whereas the activation volume analysis reflects solvation changes in the case of homogeneous processes [14]. Specifically, thermodynamic solubility data gives information on the initial state interphase transfer, and solvent effects on the transition state can be derived from the observed rate constants [13]. In this contribution, we applied the described approaches to investigate the solvent effects in the case of base hydrolysis of a series of hydrophobic high-spin iron(II) chelates with the amino acid Schiff's bases.

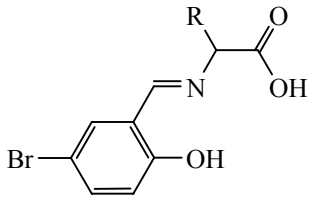
EXPERIMENTAL

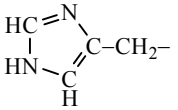
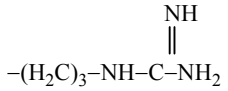
The solid complexes of Fe(II) with the Schiff's base of amino acids were prepared by mixing aqueous solutions of the respective amino acids (L-alanine, L-phenylalanine, L-aspartic acid, L-histidine, or L-arginine) with equimolar amount of 5-bromosalicylic aldehyde in the hot solution in ethanol. The resulting

[1] The text was submitted by the authors in English.

Schiff's bases were then treated with aqueous solution of equimolar amount of ferrous ammonium sulfate. In order to avoid oxidation of Fe(II) and formation of $Fe(OH)_3$, a few drops of glacial acetic acid were added [3, 4, 15]. The resulting solution was stirred during 8 h under nitrogen stream. The precipitated complexes were filtered off and washed successively with water-ethanol mixture and diethyl ether. Then, the complexes were pre-dried at a water bath and then dried over P_2O_5, under reduced pressure. Finally, the isolated complexes were recrystallized from water–ethanol mixture [3]. The complexes composition was confirmed by CHN microanalysis, IR, and UV-vis spectroscopy. The stability of solutions was monitored during at least one month in the presence of persulfate or dithionite. When the so incubated solutions of the complexes were treated with NaOH under nitrogen, green precipitate of $Fe(OH)_2$ was formed, indicating the presence of Fe(II) in the solution. In the course of kinetic experiments (see details below), the intense violet color of the complex disappeared, and the solution turned colorless. Some green colloidal particles of $Fe(OH)_2$ formed initially turned pale yellow and then precipitated as brown $Fe(OH)_3$ due to oxidation with dissolved oxygen. Complete information of the characterization of the prepared complexes can be found elsewhere [3].

Structures of the ligands along with the coding of ligands and the respective Fe(II) complexes are shown below.



Label		R
ligand	complex	
bsal	bsali	$-CH_3$
bsphal	bsphali	$-CH_2C_6H_5$
bsas	bsasi	$-CH_2COOH$
bsh	bshi	
bsar	bsari	

Kinetic measurements were carried out by following the decrease of absorbance at λ_{max} of the respective complex. The absorbance data were reorded with PG T+80 UV-Vis spectrophotometer equipped with 10 mm quartz cell and CRIOTERM 190 circulating ultrathermostat. The reaction was performed at large excess of the base so that the pseudo-first order kinetics was followed. It was confirmed that there was no absorption interference from other reagents. Each experiment was performed in duplicate to ensure satisfactory reproducibility of the kinetic parameters [12].

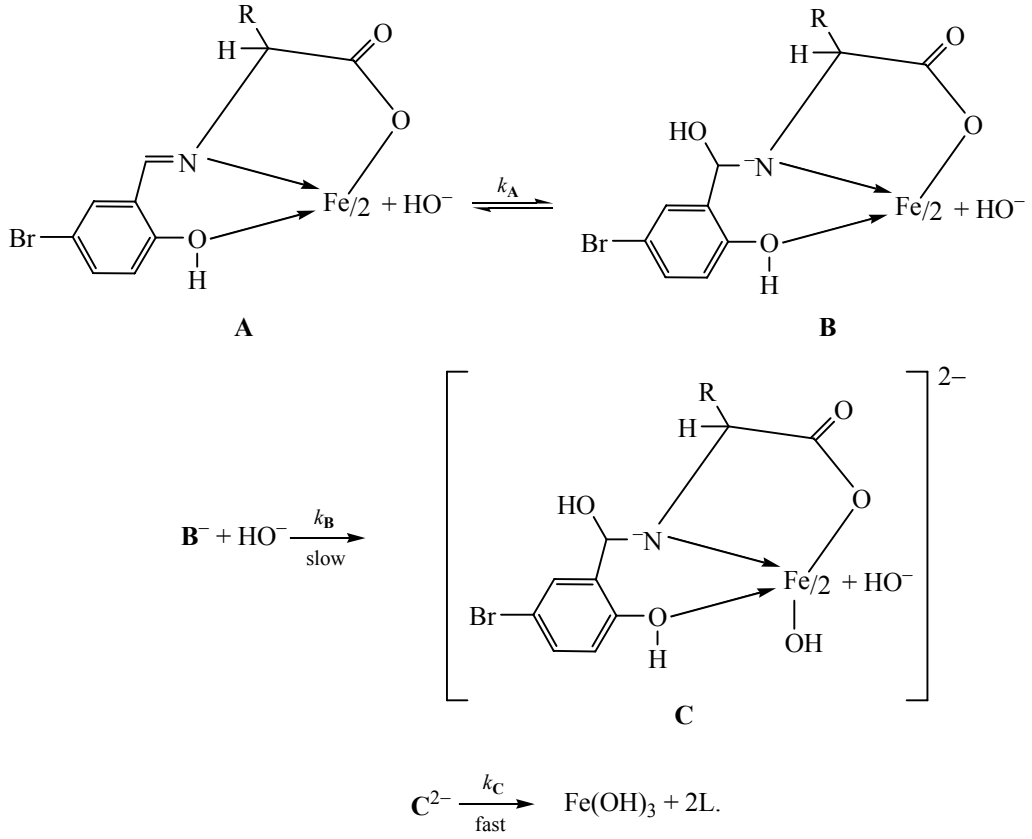
The complexes solubility was measured at 298±0.1 K by agitating a generous excess of the complex in the certain mixed solvent (water–ethanol, water–acetone, water–propanol, or water–dimethyl sulfoxide) during seven hours. That time was proved to be enough to achieve the stationary state of saturation (the spectra measured at different sampling times coincided). Then, portions of saturated solution were centrifuged, the supernatant was diluted appropriately, and the absorbance was measured at the respective λ_{max} [12, 17]. The dependence of λ_{max} on the solvent composition was found to be very small and was therefore ignored in the solubility tests. Care was taken not to heat the saturated solutions before dilution. The absorbance measured at varied dilution was treated by the least squares method to give the molar absorptivity ε.

RESULTS AND DISCUSSION

The fading of the studied solutions upon treatment with hydroxide ions indicated the complete dissociation of the complexes. In the excess of hydroxide ions and oxygen, the final products were the ligand and Fe $(OH)_3$. The rate law under the mentioned conditions followed the pseudo-first order kinetics:

$$r = k_{obs}[\text{Complex}] = (k_1 + k_2[OH^-])[\text{Complex}].$$

In the kinetic equation, k_1 is the rate constant of the complex dissociation and k_2 is the rate constant of OH^- attack; the observed rate constant is then $k_{obs} = k_1 + k_2[OH^-]$. The observed rate constants under a variety of experimental conditions are collected in Table 1, whereas the corresponding second-order hydrolysis constants k_2 are to be found in Table 2. Addition of the first hydroxide ion to the complex **A** occurred via fast pre-equilibration to give the intermediate anion **B**, as was reported by Mahmoud et al. [18]. Slow attack of the second hydroxide ion at the $\mathbf{B}^-$ was followed by fast degradation of the complex. The described mechanism scheme is as follows.



From Table 2, the values of second-order rate constant of base hydrolysis were correlated with the nature of the side substituent R in the complexes structure. The reactivity of the complexes towards hydroxide ion attack increased in the series bsari < bsali < bsphali < bshi < bsasi, following the inductive effect of the substituent. Indeed, the electron withdrawing effect of carboxylic group in bsasi was higher than that of imidazole ring in bshi and of phenyl ring in bsphali; whereas in the case of bsari, the presence of strong electron donating guanidine group lowered the complex reactivity towards OH^-.

The solubility of the prepared complexes in water and in the aqueous-organic mixed solvents (in particular, in aqueous ethanol, propanol, acetone, and dimethylsulfoxide) are collected in Table 3. From the measured solubility values, the chemical potentials of the uncharged compounds transfer from water into the mixed solvent were calculated according to the following equation:

$$\delta_m\mu^\theta = -RT\ln (S_S/S_W)$$

with S_S and S_W being solubility in the mixed solvent and in water, respectively. It was assumed that the ratio of mean activity coefficients in the aqueous and aqueous-organic media equaled unity in all cases [12]. The calculated $\delta_m\mu^\theta$ values are given in Tables 4–8.

The higher hydrophobicity of the studied Fe(II) complexes corresponded to the lower solubility in water (cf. Table 3). The negative transfer chemical potentials of the uncharged complexes (cf. Tables 4–8) could be ascribed to the hydrophobic nature of the complexes; therefore, the complexes were stabilized with increasing organic co-solvent fraction. The complexes hydrophobicity increased in the following series: bsasi < bsali < bsari < bshi < bsphali. Thus, with increasing complex volume, its solvation with organic solvent became more preferential.

The influence of organic co-solvents on the observed first-order rate constant k_{obs} for is documented in Table 3 and in Fig. 1. With increased fraction of the co-solvent, generally the rate constants of the base hydrolysis decreased. That could be attributed to the effects of destabilization or salting out of OH^- [12, 19]. Furthermore, the charge delocalization within the Fe(II) complex promoted interaction with the surrounding solvent molecules, as reflected in the enhanced solubility in the presence of

Table 1. The observed first-order rate constant ($\times 10^4$ k_{obs}, s^{-1}) of the base hydrolysis of the studied complexes in aqueous and mixed aqueous-organic solutions. $c(OH^-)$ = 3.33 mmol/L, c(complex) = 0.1 mmol/L, I = 0.01 mol/L, 298 K[a]

Complex	Co-solvent	Co-solvent fraction, vol %						
		0	10	20	30	40	50	60
bsali	EtOH	7.19	6.34	5.89	5.47	5.05	4.61	4.03
	PrOH		6.47	6.07	5.68	5.30	4.91	4.33
	acetone		6.65	6.39	6.14	5.87	5.62	5.25
	DMSO		6.86	6.61	6.40	6.18	5.97	5.62
bsphali	EtOH	8.22	7.41	6.96	6.52	6.09	5.63	5.04
	PrOH		7.57	7.17	6.79	6.38	6.01	5.51
	acetone		7.81	7.56	7.31	7.03	6.78	6.41
	DMSO		7.92	7.67	7.46	7.25	7.07	6.73
bsasi	EtOH	10.13	9.33	8.87	8.41	7.97	7.52	6.95
	PrOH		9.47	9.07	8.66	8.28	7.86	7.35
	acetone		9.63	9.37	9.17	8.91	8.67	8.30
	DMSO		9.78	9.57	9.36	9.18	8.97	8.64
bshi	EtOH	9.08	8.23	7.78	7.35	6.93	6.48	5.91
	PrOH		8.38	8.02	7.61	7.19	6.82	6.31
	acetone		8.58	8.34	8.05	7.81	7.56	7.20
	DMSO		8.76	8.56	8.37	8.16	7.96	7.65
bsari	EtOH	5.57	4.73	4.26	3.84	3.39	2.95	2.41
	PrOH		4.89	4.48	4.10	3.72	3.31	2.80
	acetone		5.07	4.81	4.56	4.29	4.05	3.69
	DMSO		5.36	5.16	4.97	4.75	4.54	4.21

[a] The error did not exceed 2%.

organic additive (Tables 4–8) [12, 20]. Hence, destabilization of OH^- ions and stabilization of the complex in the presence of increasing amounts of organic co-solvent reduced the opportunity of the reactants to combine and thus reduced the reaction rate. The effective density of dispersion interaction sites and, therefore, the observed effects increased in the series DMSO < acetone < propanol < ethanol (water revealed even less of the corresponding interaction sites than DMSO did).

In accordance with the hydrolysis mechanism, in the case of all of the systems, the transition state should more hydrophilic than the initial state, due to the ionic character of the former. Therefore, the transition state would be less stabilized by solvation at

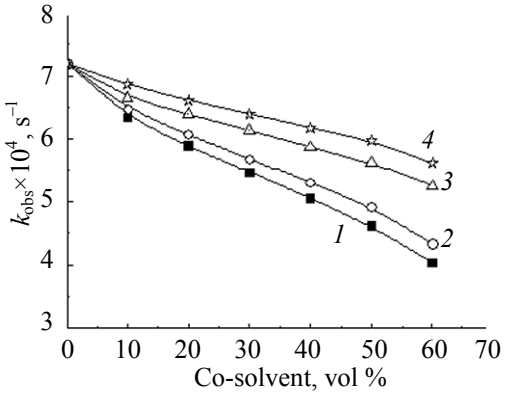


Fig. 1. The observed first–order rate constant ($k_{obs}\times10^4$, s^{-1}) of the base hydrolysis of the bsali complex in aqueous and mixed aqueous–organic solutions: (*1*) EtOH, (*2*) PrOH, (*3*) acetone, and (*4*) DMSO. $c(OH^-)$ = 3.33 mmol/L, c(complex) = 0.1 mmol/L, I = 0.01 mol/L, 298 K.

Table 2. The second-order rate constant ($\times 10^2$ k_2, mol^{-1} L s^{-1}) of the base hydrolysis of the studied complexes in aqueous and mixed aqueous-organic solutions. $c(OH^-)$ = 3.33 mmol/L, c(complex) = 0.1 mmol/L, I = 0.01 mol/L, 298 K[a]

Complex	Co-solvent	Co-solvent fraction, vol %						
		0	10	20	30	40	50	60
bsali	EtOH	17.42	16.26	15.71	15.11	14.52	13.87	13.31
	PrOH		16.51	15.94	15.57	14.98	14.57	13.98
	acetone		16.73	16.30	15.92	15.56	15.11	14.61
	DMSO		16.96	16.63	16.37	16.11	15.82	15.37
bsphali	EtOH	18.92	17.88	17.21	16.62	16.02	15.41	14.73
	PrOH		18.07	17.61	17.16	16.57	15.96	15.45
	acetone		18.33	17.98	17.51	17.16	16.73	16.14
	DMSO		18.52	18.21	17.87	17.61	17.33	16.86
bsasi	EtOH	20.63	19.51	18.97	18.42	17.81	17.21	16.62
	PrOH		19.62	19.25	18.71	18.33	17.91	17.18
	acetone		19.91	19.53	19.22	18.77	18.35	17.87
	DMSO		20.22	19.81	19.53	19.28	18.93	18.50
bshi	EtOH	19.52	18.33	17.82	17.38	16.78	16.21	15.56
	PrOH		18.48	18.10	17.65	17.21	16.80	16.23
	acetone		18.69	18.32	17.87	17.63	17.15	16.60
	DMSO		19.10	18.83	18.39	18.16	17.85	17.38
bsari	EtOH	16.21	14.91	14.06	13.78	13.24	12.70	11.94
	PrOH		15.17	14.68	14.17	13.75	13.18	12.61
	acetone		15.45	15.11	14.76	14.25	13.86	13.47
	DMSO		15.79	15.37	15.14	14.83	14.61	14.24

[a] The error did not exceed 2%.

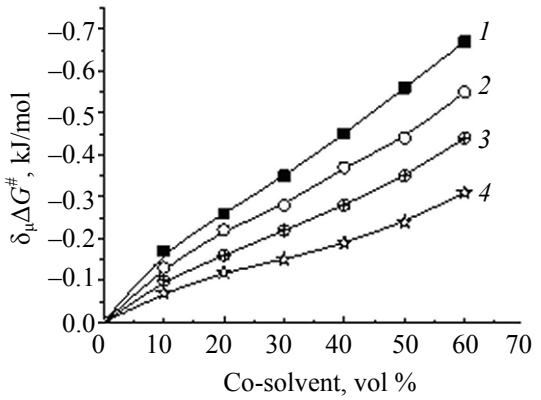


Fig. 2. The activation barrier of the interphase transfer of bsali complex from pure water to the mixed aqueous–organic medium: (*1*) EtOH, (*2*) PrOH, (*3*) acetone, and (*4*) DMSO.

increased fraction of the organic co-solvent compared with the initial state. That effect should have led to acceleration of the hydrolysis reaction, opposed to the experimental observation. Therefore, we concluded that the effect of initial state stabilization had greater impact on the overall reaction rate than the effect of transition state stabilization.

Tables 4–8 and Fig. 2 indicate that the values of activation barrier of the interphase transfer ($\delta_m\Delta G^\#$) increased with the fraction of the organic co-solvents, matching with the decrease in the values of k_2.

The solvent-induced effects on the studied reaction can be quantitatively described by parameters of the reactants transfer from water into the mixed solvent.

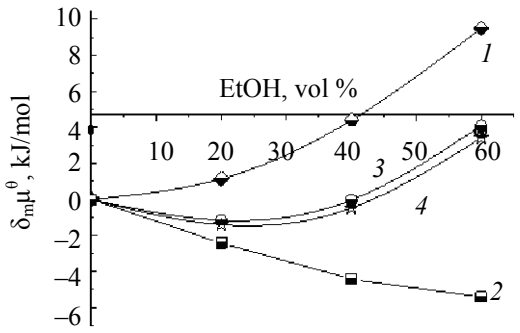


Fig. 3. The chemical potential of bsali complex, OH–, and the respective IS and TS transfer from pure water to the mixed aqueous–ethanol medium: (*1*) OH^-, (*2*) bsali, (*3*) IS, and (*4*) TS.

The respective characteristics of the initial state could be established from the solubility data, and those of the transition state could be derived taking into account the kinetic data as well. The free energy of activation as calculated with the equation below could be then used in analysis of the reactivity trends [12, 17, 21].

$$\delta_m\Delta G^{\#}_{C,P,T} = [\delta_m\Delta\mu^{\#}_{C,P,T} - \delta_m\Delta\mu^{\theta}_{C,P,T}(OH^-)] - \delta_m\Delta\mu^{\theta}_{C,P,T}(\text{compound}).$$

The transfer chemical potentials of OH^- were taken from the previous publications [12, 17, 22, 23]. Details of the initial and transition state analysis of reactivity trends followed the Abraham's assumption (Ph_4P^+, Ph_4As^+) = (Ph_4B^-) and are collected in Tables 4–8 and illustrated in Figs. 3–5. It was confirmed that the initial complexes were stabilized and the hydroxide ion was significantly destabilized upon transfer from pure

Table 3. Solubility ($\times 10^4$, mol/L) of the studied complexes in aqueous and mixed aqueous-organic solutions at 298 K

Complex	Co-solvent	Co-solvent fraction, vol%			
		0	20	40	60
bsali	EtOH	1.89	4.97	11.30	16.80
	PrOH		5.17	11.70	18.75
	Acetone		5.44	12.13	20.27
	DMSO		7.75	14.42	22.51
bsphali	EtOH	0.25	0.90	5.59	9.76
	PrOH		1.15	7.43	10.86
	Acetone		1.48	8.35	11.67
	DMSO		3.75	10.61	13.96
bsasi	EtOH	2.10	4.12	8.43	15.18
	PrOH		4.73	8.61	17.08
	Acetone		5.22	9.13	18.11
	DMSO		7.55	11.46	20.39
bshi	EtOH	0.41	1.25	2.75	7.50
	PrOH		1.41	3.11	8.23
	Acetone		1.65	3.72	8.85
	DMSO		3.91	5.89	11.15
bsari	EtOH	1.40	3.92	8.92	14.50
	PrOH		4.12	9.74	16.44
	Acetone		4.52	10.20	17.15
	DMSO		6.85	12.34	19.40

Table 4. Initial state (IS) and transition state (TS) parameters of solvent effects on reactivity trends in the case of bsali complexes at 298 K

Co-solvent	Co-solvent, vol %	$\delta_m\mu^\theta$(bsali), kJ/mol	$\delta_m\mu^\theta(OH^-)$, kJ/mol	$\delta_m\mu^\theta$(IS), kJ/mol	$\delta_m\Delta G^{\#}$, kJ/mol	$\delta_m\mu^\theta$(TS), kJ/mol
EtOH	20	–2.42	1.15	–1.15	–0.26	–1.41
	40	–4.43	4.40	–0.03	–0.45	–0.48
	60	–5.42	9.52	4.10	–0.67	3.43
Acetone	20	–2.62	4.98	2.36	–0.16	2.20
	40	–4.61	11.79	7.18	–0.28	6.90
	60	–5.88	21.03	15.15	–0.44	14.71
DMSO	20	–3.50	6.20	2.70	–0.12	2.58
	40	–5.04	14.56	9.52	–0.19	9.33
	60	–6.14	29.39	23.25	–0.31	22.94

Table 5. Initial state (IS) and transition state (TS) parameters of solvent effects on reactivity trends in the case of bsphali complexes at 298 K

Co-solvent	Co-solvent, vol %	$\delta_m\mu^\theta$(bsphali), kJ/mol	$\delta_m\mu^\theta(OH^-)$, kJ/mol	$\delta_m\mu^\theta$(IS), kJ/mol	$\delta_m\Delta G^{\#}$, kJ/mol	$\delta_m\mu^\theta$(TS), kJ/mol
EtOH	20	–3.16	1.15	–2.01	–0.23	–2.24
	40	–7.70	4.40	–3.30	–0.41	–3.71
	60	–9.05	9.52	0.47	–0.62	–0.15
Acetone	20	–4.31	4.98	0.67	–0.13	0.54
	40	–8.70	11.79	3.09	–0.24	2.85
	60	–9.53	21.03	11.5	–0.39	11.11
DMSO	20	–6.71	6.20	–0.51	–0.095	–0.61
	40	–9.29	14.56	5.27	–0.18	5.09
	60	–9.97	29.39	19.42	–0.28	19.14

Table 6. Initial state (IS) and transition state (TS) parameters of solvent effects on reactivity trends in the case of bsasi complexes at 298 K

Co-solvent	Co-solvent, vol %	$\delta_m\mu^\theta$(bsali), kJ/mol	$\delta_m\mu^\theta(OH^-)$, kJ/mol	$\delta_m\mu^\theta$(IS), kJ/mol	$\delta_m\Delta G^{\#}$, kJ/mol	$\delta_m\mu^\theta$(TS), kJ/mol
EtOH	20	–1.67	1.15	–0.52	–0.21	–0.73
	40	–3.45	4.40	0.95	–0.36	0.59
	60	–4.90	9.52	4.62	–0.54	4.08
Acetone	20	–2.26	4.98	2.72	–0.14	2.58
	40	–3.64	11.79	8.15	–0.23	7.92
	60	–5.34	21.03	15.69	–0.36	15.33
DMSO	20	–3.17	6.20	3.03	–0.10	2.93
	40	–4.21	14.56	10.35	–0.17	10.18
	60	–5.64	29.39	23.75	–0.27	23.48

Table 7. Initial state (IS) and transition state (TS) parameters of solvent effects on reactivity trends in the case of bshi complexes at 298 K

Co-solvent	Co-solvent, vol %	$\delta_m\mu^\theta$(bshi), kJ/mol	$\delta_m\mu^\theta(OH^-)$, kJ/mol	$\delta_m\mu^\theta$(IS), kJ/mol	$\delta_m\Delta G^{\#}$, kJ/mol	$\delta_m\mu^\theta$(TS), kJ/mol
EtOH	20	–2.76	1.15	–1.61	–0.23	–1.84
	40	–4.72	4.40	–0.32	–0.38	–0.7
	60	–7.21	9.52	2.31	–0.56	1.75
Acetone	20	–3.45	4.98	1.53	–0.16	1.37
	40	–5.47	11.79	6.32	–0.25	6.07
	60	–7.62	21.03	13.41	–0.4	13.01
DMSO	20	–5.59	6.20	0.61	–0.09	0.52
	40	–6.61	14.56	7.95	–0.19	7.76
	60	–8.19	29.39	21.2	–0.29	20.91

Table 8. Initial state (IS) and transition state (TS) parameters of solvent effects on reactivity trends in the case of bsari complexes at 298 K

Co-solvent	Co-solvent, vol %	$\delta_m\mu^\theta$(bsari), kJ/mol	$\delta_m\mu^\theta(OH^-)$, kJ/mol	$\delta_m\mu^\theta$(IS), kJ/mol	$\delta_m\Delta G^{\#}$, kJ/mol	$\delta_m\mu^\theta$(TS), kJ/mol
EtOH	20	–2.55	1.15	–1.40	–0.35	–1.75
	40	–4.57	4.40	–0.17	–0.5	–0.67
	60	–5.80	9.52	3.72	–0.76	2.96
Acetone	20	–2.91	4.98	2.07	–0.17	1.90
	40	–4.92	11.79	6.87	–0.32	6.55
	60	–6.21	21.03	14.82	–0.46	14.36
DMSO	20	–5.59	6.20	0.61	–0.09	0.52
	40	–6.61	14.56	7.95	–0.19	7.76
	60	–8.19	29.39	21.2	–0.29	20.91

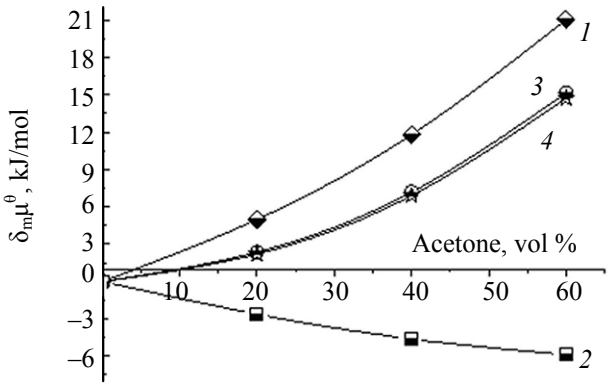


Fig. 4. The chemical potential of bsali complex, OH–, and the respective IS and TS transfer from pure water to the mixed aqueous–acetone medium: (*1*) OH^-, (*2*) bsali, (*3*) IS, and (*4*) TS.

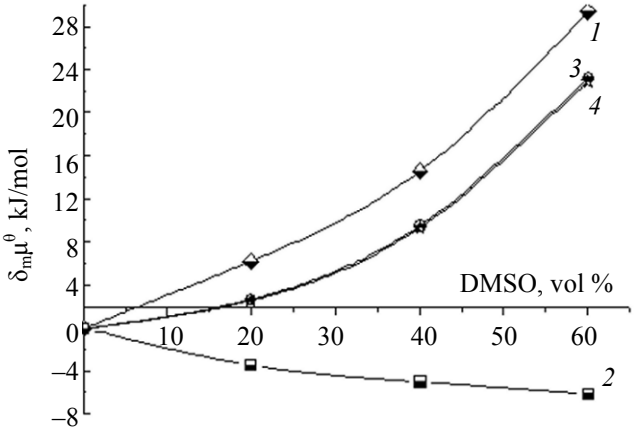


Fig. 5. The chemical potential of bsali complex, OH^-, and the respective IS and TS transfer from pure water to the mixed aqueous–DMSO medium: (*1*) OH^-, (*2*) bsali, (*3*) IS, and (*4*) TS.

water to the mixed solvent, resulting in an overall decrease in stabilization of the initial state (IS). On the other hand, the transition state (TS) was destabilized as pure water was changed to the mixed solvent. Therefore, the observed overall decrease of the rate constant could be attributed to the dominant effect of the initial state stabilization on the kinetics of base hydrolysis of the studied complexes.

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