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Effect of Bromide Salts on the Acid Hydrolysis of Anti-Bacterial Hydrophilic Schiff Base Amino Acid Iron(II) Complexes[1]

Ali M. Shaker, Lobna A. E. Nassr, Mohamed S. S. Adam, and Ibrahim M. A. Mohamed

Chemistry Department, Faculty of Science, Sohag University, Sohag, 82524 Egypt
e-mail: imaashour20080@yahoo.com

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Abstract—Salt effects on the kinetics of acid hydrolysis of some novel hydrophilic iron(II) complexes have been investigated in aqueous medium. The ligands are derived from the condensation of amino acids (glycine, L-alanine, L-leucine, L-isoleucine, DL-methionine, DL-serine or L-phenylalanine) and sodium 2-hydroxybenzaldehyde-5-sulfonate. The reaction was studied under conditions of pseudo first order kinetics. The general rate equation was suggested as follows: rate = k_{obs}[complex], where $k_{obs} = k_2[H^+]$. The reaction rate decreases with an increase of the salt concentration.

Keywords: iron(II) complex, amino acid, kinetics, salt effect, acid hydrolysis

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INTRODUCTION

Over the past few years, Schiff base complexes show good activity in catalysis [1], and high biological activity, such as antibacterial, antifungal, anticancer, and herbicidal applications [2–4]. Schiff bases derived from sodium 2-hydroxybenzaldehyde-5-sulfonate are used as catalytic antioxidants [5]. Comparatively, very little effort has been expended to study the kinetics of Schiff base amino acid iron(II) complexes [6–8] despite their importance. The effects of the reaction medium on reactivity have been established and discussed for a variety of reactions involving inorganic complexes in aqueous salt solutions [9, 10]. Therefore, in this work we study the effect of substituent and salts on the acid hydrolysis of anti-bacterial Schiff base amino acid iron(II) complexes.

EXPERIMENTAL

Reagents and instrumentation. All the used amino acids, hydrochloric acid, tetraethylammonium and tetramethylammonium bromides, potassium bromide, lithium bromide and $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ were of analytical grade purchased from Sigma Aldrich, and sodium 2-hydroxybenzaldehyde-5-sulfonate was prepared according to literature procedure [11]. The studied complexes were prepared by the method of Shaker [12]. 2 mmol (0.448 g) of sodium 2-hydroxybenzaldehyde-5-sulfonate in deionized water (20 mL) was added dropwise to an equimolar solution of amino acid in deionized water (complex **I**, 0.15 g glycine in 10 mL; complex **II**, 0.178 g L-alanine in 10 mL; complex **III**, 0.262 g L-leucine in 15 mL; complex **IV**, 0.262 g L-isoleucine in 15 mL; complex **V**, 0.298 g DL-methionine in 15 mL; complex **VI**, 0.21 g DL-serine in 10 mL; and complex **VII**, 0.33 g L-phenylalanine in 10 mL) and the mixture was stirred at 100°C for 3 h to give yellow color. Then the obtained ligand solution was mixed with an equimolar aqueous solution of ferrous ammonium sulfate. In order to avoid the oxidation of ferrous to ferric, a few drops of glacial acetic acid were added [12, 13]. The resulting solution was stirred at 40°C for 10 h (its color became deep violet) and evaporated at room temperature. The solid obtained was filtered-off, washed several times with ether, and crystallized from ethanol–water mixture (2 : 1). All the complexes were prepared by similar procedure. Full details of characterization of the investigated complexes and their anti-bacterial activity can be found in our previous work [14]. The chemical structure of the studied complexes showed in Scheme 1.

RESULTS AND DISCUSSION

The effect of $[H^+]$ on the hydrolysis rate of the prepared Fe(II) Schiff base amino acid complexes was

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

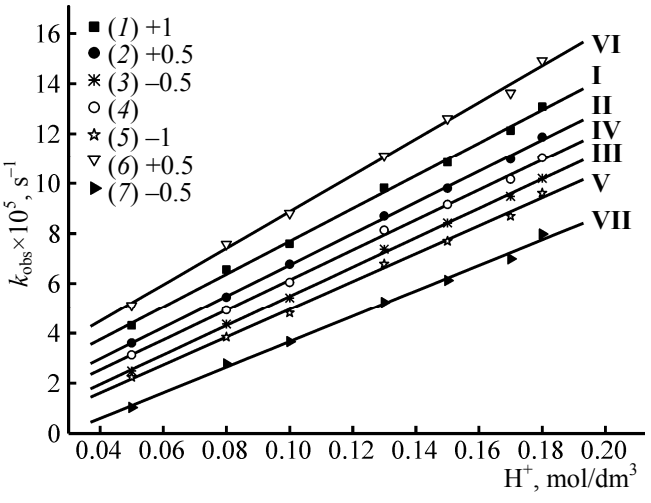


Fig. 1. The relationship between $[H^+]$ and k_{obs} values for acid hydrolysis of investigated complexes in aqueous medium with [complex] = 1.67×10^{-3} mol/dm^3, I = 0.5 mol/dm^3, T = 298 K.

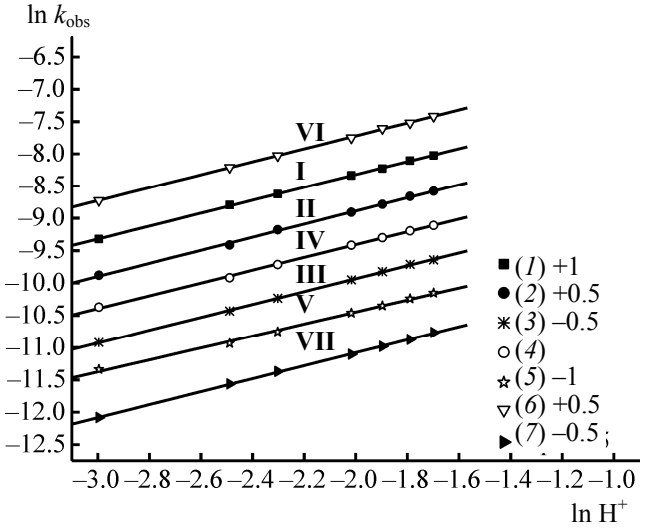


Fig. 2. Plots of ln k_{obs} as a function of ln $[H^+]$ in aqueous solution with complexes in aqueous medium with [complex] = 1.67×10^{-3} mol/dm^3, I = 0.5 mol/dm^3, T = 298 K.

studied within the range of 0.05 to 0.18 mol/L at [complex] = 1.67×10^{-3} mol/L, constant ionic strength = 0.5 mol/L by the inert solution of KNO_3 and 298 K. The observed first order rate constant values, (Table 1), evaluated from the slopes of the first order rate plots (logarithm of absorbance versus time) at different concentrations of HCl indicate the acid hydrolysis rate of the investigated complexes. Linear plots are shown in Fig. 1 and demonstrate a good correlation with the following equation:

$$k_{obs} = k_2[H^+].$$

The overall rate law for the investigated reaction under the adopted conditions of pseudo first order kinetics can be represented as follows:

$$\text{rate} = k_{obs}[\text{complex}] = (k_2[H^+])[\text{complex}].$$

To obtain more details about the recent reaction mechanism, the value of the reaction order (n) for $[H^+]$ was determined by a least-squares procedure from the slopes of the linear plots of ln k_{obs} vs. ln $[H^+]$ (Fig. 2) according to the following equation:

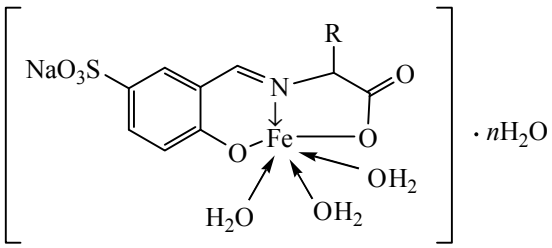
$$\ln k_{obs} = \ln k' + n\ln [H^+],$$

where k' is the value intersected on the ordinate axis. The values of reaction order (n) were found to be nearly one (Table 2) for the different investigated complexes indicating that there is only one slow step.

The characteristic band for the investigated complexes in the UV/visible spectra lies at λ_{max} near 500 nm. On the addition of $[H^+]$, its untensity decreases, Fig. 3 and the color of the complex slowly fades. These spectrophotometrically and visually observable changes allowed us to suggest the following mechanism for the acid hydrolysis (Scheme 2).

In the acidic medium (pH ≤ 2) in which the complexes exist mainly as their conjugate acids, the acid hydrolysis rates of these compounds increase with

Scheme 1. Structure of investigated complexes



Complex	R	n	Complex	R	n
I	H	1	**V**	$CH_2CH_2SCH_3$	3
II	CH_3	1	**VI**	CH_2OH	3
III	$CH_2CH(CH_3)_2$	1	**VII**	CH_2Ph	3
IV	$CH(CH_3)CH_2CH_3$	1			

Table 1. The observed first order rate constant ($k_{obs} \times 10^5$, s^{-1}) values for the acid hydrolysis of studied complexes in aqueous medium at different $[H^+]$, [complex] = 1.67×10^{-3} mol/dm^3, I = 0.5 mol dm^{-3} and T = 298 K

Complex / $[H^+]$	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**
0.05	3.3	3.1	2.99	3.13	3.24	3.62	2.53
0.08	5.56	4.95	4.86	4.93	4.84	6.07	4.27
0.10	6.59	6.27	5.93	6.05	5.81	7.3	5.16
0.13	8.82	8.2	7.88	8.13	7.78	9.61	6.75
0.15	9.84	9.3	8.92	9.15	8.69	11.11	7.63
0.17	11.13	10.48	9.98	10.16	9.69	12.13	8.49
0.18	12.08	11.37	10.7	11.03	10.6	13.42	9.48
$k_2 \times 10^4$, $M^{-1} s^{-1}$	6.60	6.30	5.90	6.04	5.61	7.34	5.14

decreasing pH. Thus, in these solutions, the hydrolysis mechanism would involve the conversion of the (CH=N) group to its conjugate acid ($CH=NH^+$) by a rapid pre-equilibrium followed by a slow attack of water. This argument has a reasonable theoretical base that the anil carbon assumes considerable carbonium ion characteristics induced by conjugate acid formed in these acidic media and that it is more susceptible to nucleophilic attack by water [15]. After this, the protonated complex rapidly decays into the final products, which are suggested to be the amino acid and sodium 2-hydroxybenzaldehyde-5-sulfonate with the oxidation of Fe(II) to Fe(III) under the influence of the dissolved oxygen in the solution [16].

The observed first order rate constants of the hydrolysis of the studied complexes in aqueous medium increase in the following order: **VII** < **V** < **III** < **IV** < **II** < **I** < **VI.**

This behavior is similar to the order of ascending hydrophilicity of these complexes as was proved by us by solubility measurements [17]. Hydrophilicity increases in the following order: **VII** < **V** < **III** < **IV** < **VI** < **II** < **I**.

The reactivity trend would be due to the opposite desolvation of the less hydrophilic ligands and hence their Fe(II) salicylidene amino acidate Schiff base complexes. Thus the decreasing activity coefficient of the hydrophilic complexes may retard the attack of water on the polar azomethine group of the complexes and thus reduce the reactivity.

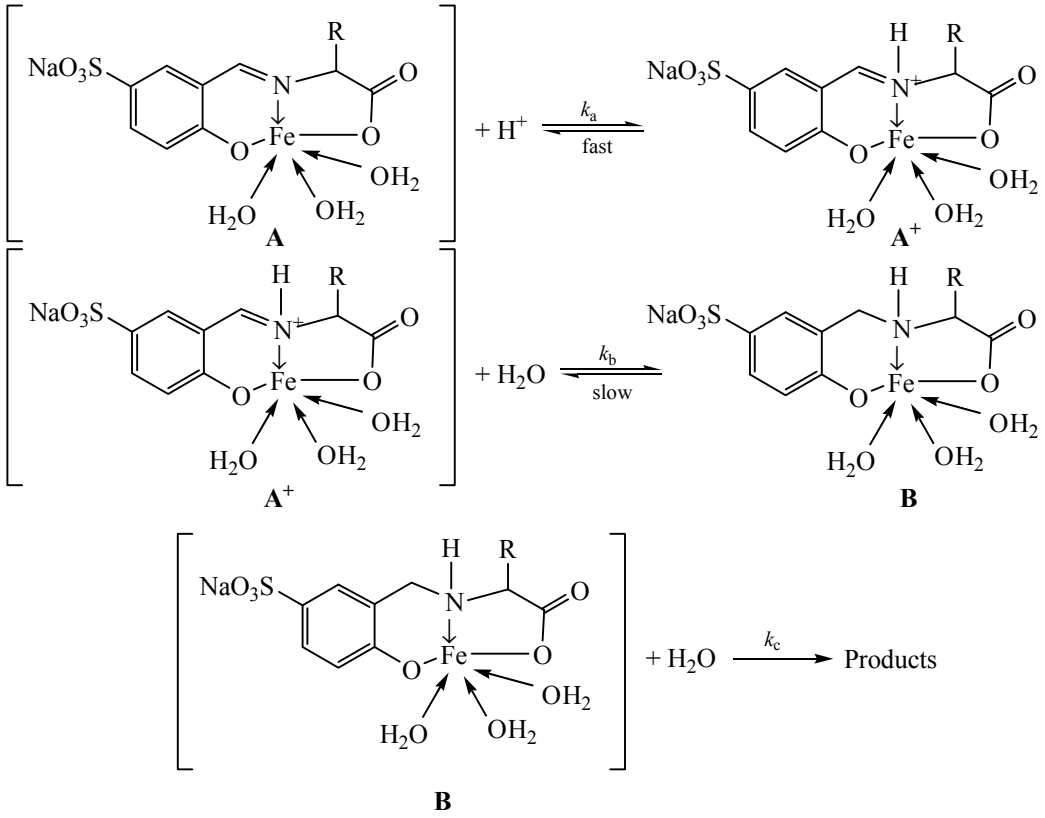
It seems that the reactivity is controlled by hydrophobic/hydrophilic characteristics of the studied complexes. In general, the reactivity decreases with a decrease of the hydrophilicity of the complex because of its less stabilization in aqueous solutions. The unexpectedly high reactivity of complex **VI** should be assigned to the side chain effects. The side chain is polar in serine and nonpolar in glycine and alanine. Excess protons surrounding the CH_2–OH bond cause more polarization of this bond and, thus, more strong electron-withdrawing effect of the CH_2OH group in the serine moiety of complex **VI**. This effect would decrease the electron density of the azomethine nitrogen (anil), thereby increasing the polarizability of the anil carbon group and hence faster attack of water which is the rate determining step.

The observed rate constants were calculated and tabulated in Figs. 4–8 for different salts and salt concentrations.

Table 2. The reaction order (n) and k' values, as determined from the plots ln k_{obs} vs. ln $[H^+]$ for the acid hydrolysis of the complexes **I–VII**. [complex] = 1.67×10^{-3} mol/L, I = 0.50 mol/L, T = 298 K

Complex	Reaction order	$k' \times 10^4$
I	1.00	6.60
II	1.01	6.35
III	0.99	5.86
IV	0.98	5.90
V	0.93	5.04
VI	1.00	7.41
VII	1.01	5.18

Scheme 2. Suggested mechanism of acid hydrolysis of investigated complexes



In the studied acid hydrolysis reactions, the reactivity trends against inert salt effects are indeed strikingly different and complicated. The observed decrease in the reactivity with increasing salt concentration agrees with the cationic nature of the reactants in the rate determining step and confirms the suggested mechanism. The presence of salt decreases the solubility of the hydrophilic protonated complex

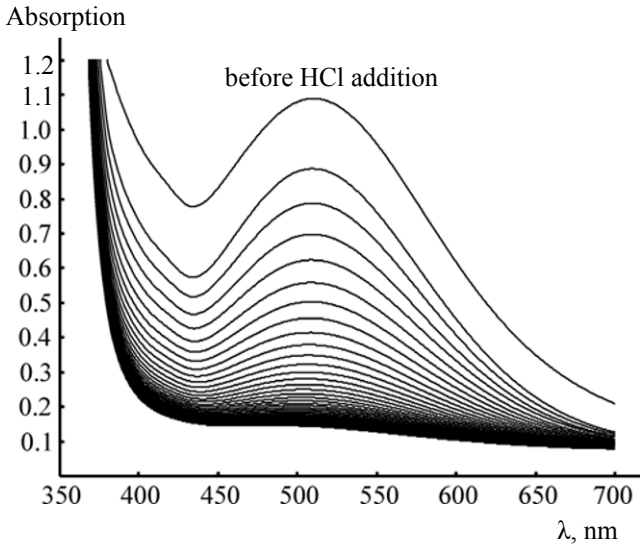


Fig. 3. UV spectra of complex **VI** before and after addition of HCl in water. [complex] = 1.67×10^{-3} mol/L, [HCl] = 0.1 mol/L, I = 0.5 mol/L, T = 298 K, interval time = 1 min.

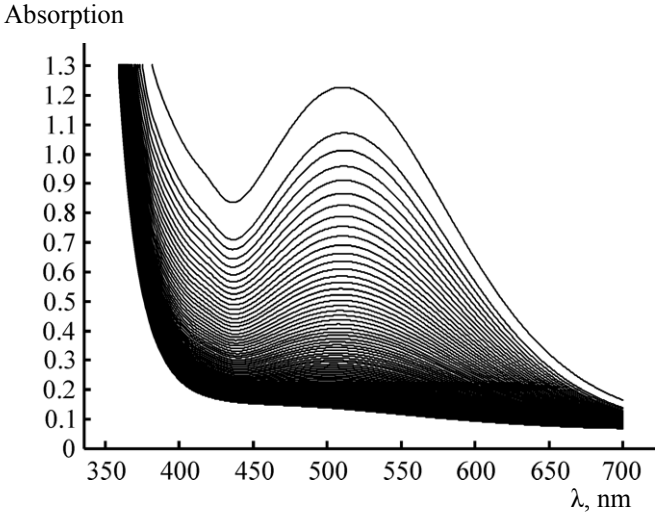


Fig. 4. Repeated spectral scans of complex **V** before and after addition of HCl in aqueous media at [complex] = 1.67×10^{-3} mol/dm^3, [HCl] = 0.1 mol/dm^3, I = 0.5 mol/dm^3, T = 298 K, interval time = 1 min.

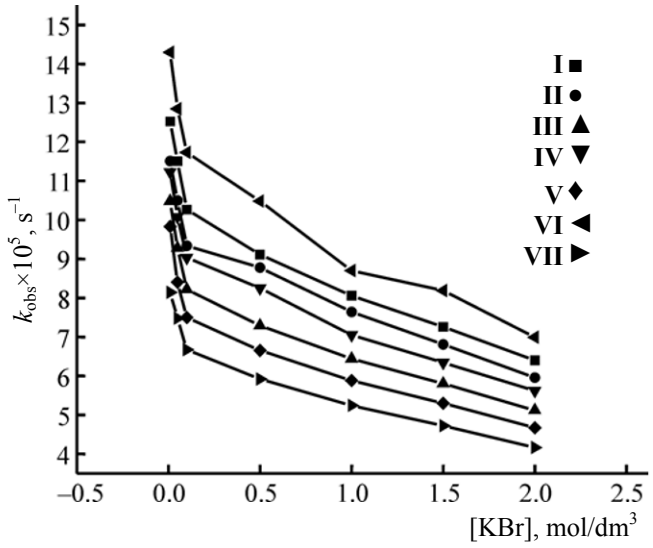


Fig. 5. Dependence of k_{obs} for the acid hydrolysis of the investigated complexes on [KBr] at [complex] = 1.67 × 10^{-3} mol/dm^3, [H^+] = 0.13 mol/dm^3, T = 298 K.

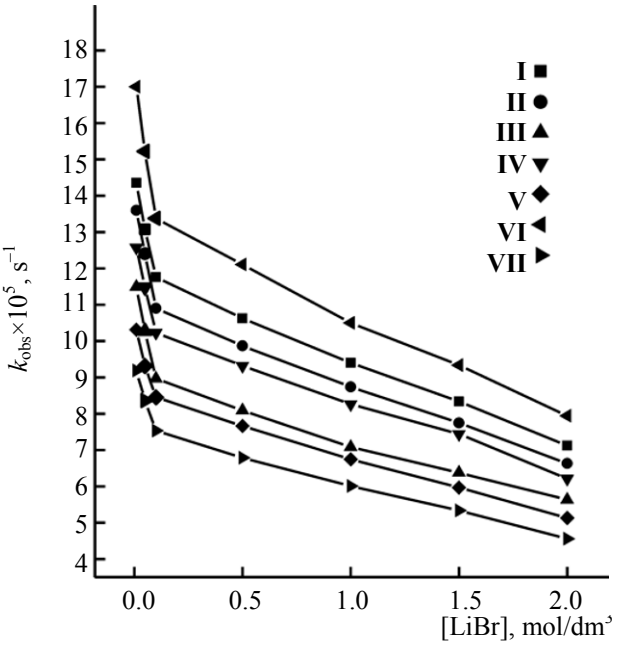


Fig. 6. Dependence of k_{obs} for the acid hydrolysis of the investigated complexes on [LiBr] at [complex] = 1.67 × 10^{-3} mol/dm^3, [H^+] = 0.13 mol/dm^3, T = 298 K.

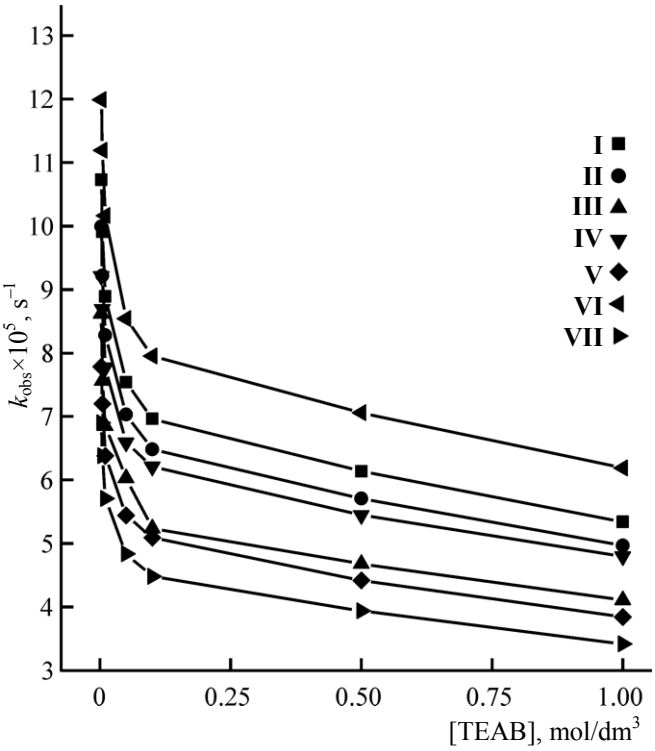


Fig. 7. Dependence of k_{obs} for the acid hydrolysis of the investigated complexes on [TEAB] at [complex] = 1.67 × 10^{-3} mol/dm^3, [H^+] = 0.13 mol/dm^3, T = 298 K

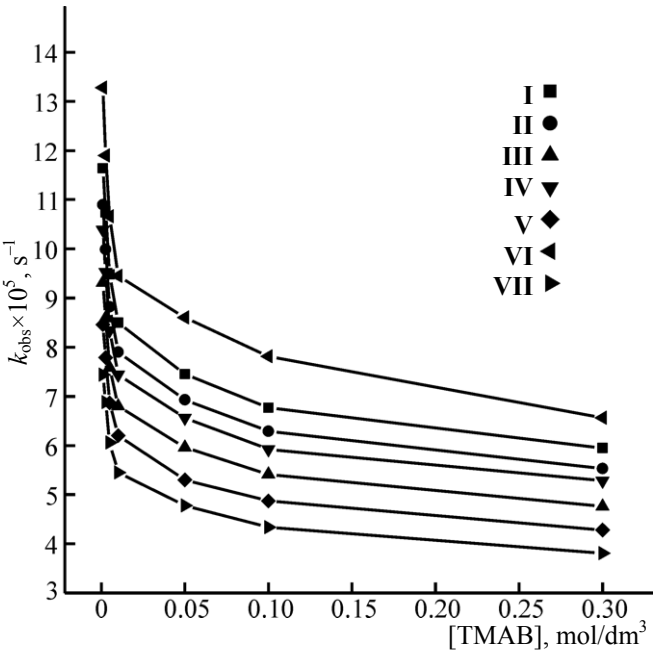
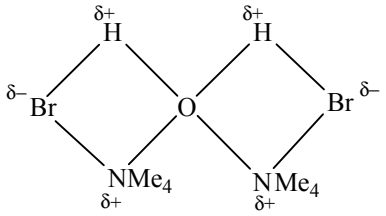


Fig. 8. Dependence of k_{obs} for the acid hydrolysis of the investigated complexes on [TMAB] at [complex] = 1.67 × 10^{-3} mol/dm^3, [H^+] = 0.13 mol/dm^3, T = 298 K.

($\mathbf{A}^+$) in the rate determining step. The hydrophobic hydration characteristics of TEAB and TMAB retard the attack of water on the anil group of the investigated complexes in the slow step of the suggested mechanism. This effect would lead to a significant decrease of the observed rate constant of the acid hydrolysis of the studied complexes. This behaviour could be illustrated by the formation of a cyclic quadrupole interaction between the hydrophobic salts ion pairs and the solvent as follows [18]:



The formed salt–solvent quadruples would distort the voids of the hydrogen bonded water molecules; this, in turn, increases the activity coefficients of the hydrophilic complexes, thus stabilizing them and lowering their reactivity. This argument would present more reasonable interpretation for the observed further decrease of reactivity of the less hydrophilic complexes in the presence of hydrophobic salts TEAB and TMAB. Again, it would be the ion pairs formed between these hydrophobic salts TMAB and TEAB and the complexes cations $\mathbf{A}^+$ in the rate determining step.

The reason for substantial reduction of the reactivity against water attack and hence the reactivity of the acid hydrolysis reaction as a whole compared with the decrease of reactivity in the presence of the alkali metal cations (Li^+ and K^+), is that the bulky R groups in the added TMAB and TEAB salts would sterically hinder the approach of the reactants (the cationic intermediate precursor and water molecule).

CONCLUSIONS

Acid hydrolysis of new hydrophilic iron(II) complexes has been investigated in aqueous medium under conditions of pseudo first order kinetics. The reactivity of the complexes decreases with an increase of the salt concentration. The reaction mechanism including one slow rate-determining step is proposed.

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