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Salts and Structural Effects on the base Catalyzed Hydrolysis of some Novel and Pharmacologically Active Iron (II) Azomethine Amino Acid Complexes.

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Abstract: The effect of salts on the reactivity of base hydrolysis of Fe(II) chelates bis(naphthylidene alanate) (nali), bis(naphthylidene phenylalanate) (nphali), bis(naphthylidene aspartate) (nasi), (naphthylidene histidinate) (nhi), bis(naphthylidene arginate) (nari) has been investigated in aqueous media containing alkali metal halides viz. LiBr, NaCl, KBr, Tetramethylammonium bromide (TMAB), Tetraethylammonium bromide (TEAB) and Tetrabutylammonium bromide (TBAB). The suggested mechanism of the base hydrolysis reaction involves the parallel attack of OH- ion on Fe^{2+} central atom attached to a singly bonded OH^- ligand and dissociation of the first ligand as rate determining step. Generally, the presence of the salt markedly enhances the rate compared to its absence. This behavior agrees with the anionic nature of the transient species. With increasing added NaCl and NaBr, the rate of the reaction decreases. But in case of TMAB, TEAB and TBAB salts, the rate increases and then decreases on increasing their concentration.

Keywords: Acid-base hydrolysis, kinetics, iron(III) amino acid complexes, azomethane

1.Introduction

Salt effects on reactivity in solution have been of considerable interest for a very long time, indeed since studies of so called "cation catalysis" of reactions between organic substrates and such nucleophiles as hydroxide and thiocyanate in the early years of this century. Brønsted, following suggestions by Bjerrum, rationalised salt effects on reactivity in terms of activity coefficients (Debye-Huckel) of initial and transition states. Brarnsted and Livingston subsequently collated ionic strength effects on reactivities of inorganic complexes in the form of the diagrams which bear the latter's name.

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 [1]. Despite the importance of these salt effects, the subject has been long neglected in the literature. As is well known, water is highly associated via hydrogen bonding, and various solutes / co-solvents can increase or decrease the distribution of such hydrogen bonds. The presence of salts in the reaction medium affects on the rate of a reaction and modifies the solubility of the reactants. Therefore, it was decided to carry out an extensive investigation of such salt effect which, in turn, may provide useful information on the nature of the transition state in the mechanism of base hydrolysis reactions of the title compounds and the hydrophobic character of the ligands/complexes. The prepared Schiff base amino acid complexes are good chelating agents [2,3] biologically active [4,5] and cytotoxic [6] agents. In addition, Schiff bases of amino acids complexes are considered to constitute new kinds of potential antibacterial and anticancer reagents [7]. These are a new series of important Fe(II) chelates of Schiff bases derived from 2-hydroxy-1-naphthaldehyde (HN) and some amino acids viz. L-alanine (nali), L-phenylalanine (nphali), L-aspartic acid (nasi), L-histidine (nahi) and L-arginine (nari). Thus this study aims to elucidate the details of the salt effect on the base hydrolysis rate of the above complexes, exhibited by alkali metal cations, on one hand, and hydrophobic tetraalkylammonium cations, on the other hand [8]. The behavior of these Fe(II) complexes in alkaline solutions containing varying amounts of different salts is of considerable interest.

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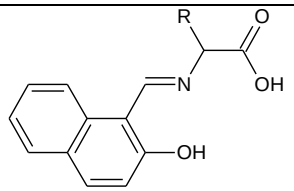
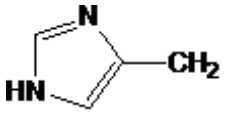
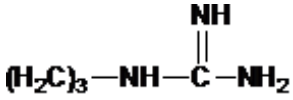


Acronym		R
Ligand	Complex	
nal	nali	CH_3
nphal	nphali	$CH_2C_6H_5$
nas	nasi	CH_2COOH
nh	nhi	
nar	nari	

Scheme (1): Structures and abbreviations of the Schiff base ligands and abbreviations of their corresponding complexes.

2. Experimental Section

The iron(II) complexes were prepared by the literature method [3, 4]. An aqueous solution of the α-amino acid was mixed with a hot ethanolic solution of the aldehyde in stoichiometric amounts. The resulting amino acid Schiff base ligand was then stabilized by chelation to iron(II) by adding an aqueous solution of ferrous ammonium sulfate in an equivalent ratio. To avoid the Fe(II) oxidation, five to six drops of glacial acetic acid were added. The resulting solution was stirred magnetically for 14 h with continuous N_2 bubbling. The isolated complexes were recrystallized from water–ethanol solutions. The composition of the complexes was established by CHN microanalysis, IR, UV–vis spectral analyses. All gave satisfactory CHN microanalysis (c.f table 1) [4]. Full details of characterization of the present complexes can be found in our previous publication [4]. The purity of these complexes was checked spectrophotometrically [3,4,9,10], by confirming that the kinetics were exactly first-order up to 90% of the reaction progress, and that the obtained rate constants agreed well with the reported values. Solutions were tested, over a long period of time, at least a month, for the stability of Fe(II) cation by their resistance toward reduction with by dithionite. Again, if an aged complex solution was treated with NaOH under N_2, a green precipitate of $Fe(OH)_2$ formed, indicating the presence of Fe(II) in the complex solution used in the kinetic runs. It was observed that in these runs, the intense violet color of the complex solution fades during the course of each reaction. The solution then turns colorless and some traces of green colloidal particles of $Fe(OH)_2$ turning pale yellow appear. Finally, the sodium hydroxide and the salts used were of the purest commercially available grades. Kinetic experiments were carried out following the decrease in absorbance at λ_{max}, the absorption maxi-mum of the tested complex, in a 1 cm thermostatted cell of a Jasco automatic scanning spectrophotometer with a Jasco cell and wavelength programmer. There was no interference from any other reagents at this wavelength. The reactants, i.e., the complex and hydroxide, were mixed so that the reaction the hydrolysis product precipitates as brown $Fe(OH)_3$ by oxidation with O_2 dissolved in solution long after the end of the kinetic run.

In order to investigate the effect of the added salt on the rate of the aquation reaction of the investigated Schiff base amino acid Fe(II) complexes, the reaction was carried out in the presence of different salts with different nature of hydrophobicity, viz. LiBr, NaCl, KBr, Tetramethylammonium bromide (TMAB), Tetraethylammonium bromide (TEAB) and Tetrabutylammonium bromide (TBAB) with different concentrations, [complex] = 1 x 10^{-4} mol dm^{-3}, [OH^-] = 5.83 x 10^{-3} mol dm^{-3} and 298 K.

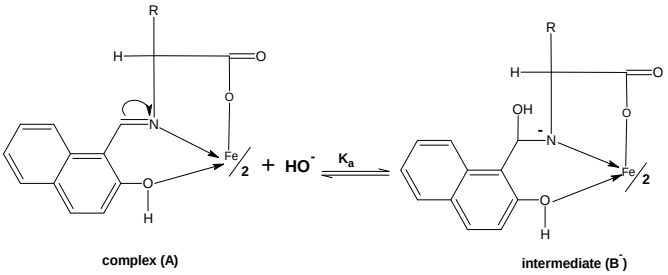
3. Result and discussion

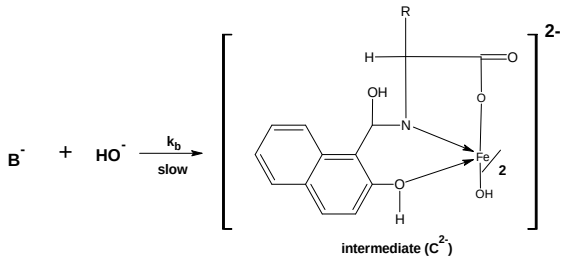
Fading of color of the solutions of the Fe(II) amino acid Schiff base complexes by hydroxide ion indicates that the complete dissociation occurs. In the presence of excess hydroxide ion and oxygen, the ultimate product, in addition to the ligand, is $Fe(OH)_3$. The overall rate law for the investigated reaction under the adopted conditions of pseudo first order kinetics can be represented as follows:

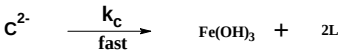
$$Rate = k_{obs}[complex] = (k_1 + k_2[OH^-])[complex]$$

Graphics should be inserted where they are first mentioned (unless they are equations, which appear in the flow of the text). They can be single column or double column as appropriate.

The k_1 term is assigned to rate determining dissociation of the investigated complexes and the k_2 term to rate determining attack by OH^- at the compounds, where $k_{obs} = k_1+k_2$ $[OH^-]$. The first hydroxide ion adds to the electrophilic carbonium of the polarized azomethine in a fast pre-equilibrium step [10-13]. The second hydroxide ion slowly attacks the central iron atom in the intermediate B^{2-} (cf. The following mechanism) followed by degradation of the complex.







Scheme (2): The suggested Mechanism for the base hydrolysis reaction.

Table (1): Analytical and physical data for the Schiff base amino acid ligands and their Fe(II) complexes.

Comp.	Empirical Formula (Formula Weight)	Analysis Found (Calculated)		
		C	H	N
nal	$C_{14}H_{13}NO_3$ (243.254)	69.25 (69.12)	5.17 (5.39)	5.61 (5.76)
nali	$C_{28}H_{28}FeN_2O_8$ (576.37)	58.50 (58.34)	4.67 (4.90)	4.88 (4.86)
nphal	$C_{20}H_{17}NO_3$ (319.346)	75.35 (75.22)	5.21 (5.37)	4.45 (4.39)
nphali	$C_{40}H_{34}FeN_2O_7$ (710.54)	67.85 (67.61)	4.57 (4.82)	3.76 (3.94)
nas	$C_{15}H_{13}NO_5$ (287.168)	62.81 (62.73)	4.63 (4.56)	4.72 (4.88)
nasi	$C_{30}H_{26}FeN_2O_{11}$ (646.38)	56.01 (55.74)	3.92 (4.05)	4.21 (4.33)
nh	$C_{17}H_{15}N_3O_3$ (309.32)	66.13 (66.01)	4.72 (4.89)	13.44 (13.59)
nhi	$C_{17}H_{21}FeN_3O_7$ (435.22)	46.83 (46.91)	4.72 (4.86)	9.58 (9.66)
nar	$C_{17}H_{20}N_4O_3$ (328.37)	62.29 (62.18)	6.05 (6.14)	17.21 (17.07)
nari	$C_{34}H_{44}FeN_8O_9$ (764.62)	53.64 (53.40)	5.72 (5.80)	14.43 (14.66)

Table (2): Observed first order rate constant values (10^3 $k_{obs.}$, s^{-1}) for the base hydrolysis of nali complex in different added molar concentrations of salts in aqueous medium, at [nali] = 1 x 10^{-4} mol dm^{-3}, $[OH^-]$ = 5.83 x 10^{-3} mol $dm^{-3}$and 298 K :

[salt]	NaCl	KBr	LiBr	TMAB	TEAB	TBAB
0.005				9.79	9.83	9.86
0.01				9.84	9.92	10.06
0.05				10.15	10.28	10.61
0.10	10.15	9.98	10.54	10.02	9.87	9.75
0.15	10.31	10.08	10.67	9.78	9.59	9.41
0.20	10.48	10.21	10.85			
0.30	10.82	10.42	11.25			
0.50	11.48	10.83	11.91			
0.70	12.11	11.18	12.53			
1.00	12.95	11.74	13.37			
1.20	13.63	12.18	14.10			

Table (3): Observed first order rate constant values (10^3 $k_{obs.}$, s^{-1}) for the base hydrolysis of nphali complex in different added molar concentrations of salts in aqueous medium, at [nphali] = 1 x 10^{-4} mol dm^{-3}, [OH^-] = 5.83 x 10^{-3} mol dm^{-3} and 298 K :

salt [salt]	NaCl	KBr	LiBr	TMAB	TEAB	TBAB
0.005				11.35	11.43	11.47
0.01				11.16	11.31	11.39
0.05				10.33	10.68	10.92
0.10	11.82	11.71	12.03	9.41	10.07	10.45
0.15	11.91	11.78	12.20	8.58	9.35	9.97
0.20	12.03	11.86	12.38			
0.30	12.37	12.03	12.76			
0.50	12.94	12.38	13.55			
0.70	13.55	12.72	14.31			
1.00	14.42	13.18	15.22			
1.20	14.91	13.44	15.96			

Table (4): Observed first order rate constant values (10^3 $k_{obs.}$, s^{-1}) for the base hydrolysis of nasi complex in different added molar concentrations of salts in aqueous medium, at [nasi] = 1 x 10^{-4} mol dm^{-3}, [OH^-] = 5.83 x 10^{-3} mol $dm^{-3}$and 298 K :

salt [salt]	NaCl	KBr	LiBr	TMAB	TEAB	TBAB
0.005				9.63	9.88	10.12
0.01				9.75	10.02	10.35
0.05				10.11	10.38	10.97
0.10	13.26	13.11	13.45	10.42	10.76	11.66
0.15	13.41	13.18	13.69	10.69	11.10	12.28
0.20	13.56	13.27	13.94			
0.30	13.92	13.42	14.47			
0.50	14.57	13.73	15.39			
0.70	15.25	14.05	16.28			
1.00	16.20	14.54	17.68			
1.20	16.85	14.97	18.54			

Table (5): Observed first order rate constant values (10^3 $k_{obs.}$, s^{-1}) for the base hydrolysis of nhi complex in different added molar concentrations of salts in aqueous medium, at [nhi] = 1 x 10^{-4} mol dm^{-3}, [OH^-] = 5.83 x 10^{-3} mol dm^{-3} and 298 K :

[salt]	NaCl	KBr	LiBr	TMAB	TEAB	TBAB
0.005				15.27	15.41	15.54
0.01				15.39	15.55	15.71
0.05				15.77	15.92	16.22
0.10	15.96	15.87	16.14	16.02	16.23	16.69
0.15	15.87	15.72	16.10	16.41	16.57	17.22
0.20	15.79	15.64	16.02			
0.30	15.60	15.41	15.87			
0.50	15.32	15.06	15.65			
0.70	15.05	14.64	15.42			
1.00	14.58	14.11	15.13			

Table (6): Observed first order rate constant values (10^3 $k_{obs.}$, s^{-1}) for the base hydrolysis of nari complex in different added molar concentrations of salts in aqueous medium, at [nari] = 1 x 10^{-4} mol dm^{-3}, [OH^-] = 5.83 x 10^{-3} mol dm^{-3} and 298 K :

salt [salt]	NaCl	KBr	LiBr	TMAB	TEAB	TBAB
0.005				7.88	7.95	8.11
0.01				8.01	8.10	8.34
0.05				8.57	8.74	9.04
0.10	8.27	8.12	8.42	8.38	8.29	8.21
0.15	8.32	8.21	8.53	7.75	7.57	7.44
0.20	8.45	8.28	8.68			
0.30	8.67	8.43	8.94			
0.50	9.07	8.75	9.35			
0.70	9.47	9.08	9.83			
1.00	10.11	9.54	10.54			
1.20	10.53	9.87	11.11			

The data depicted in Tables (2-6) show an abrupt increase of the rate constant upon adding salts with low concentrations. This behaviour is in accord with suggestions presented by Brønsted–Bjerrum and Livingston and also to the suggested mechanism [14] that the slow step involves the formation of negatively charged complex conjugate base Moreover, this trend of alkali metal halides solutions agrees with the report [15] that the rates of bimolecular organic reactions in water is enhanced dramatically by salting out reagents like KBr, NaCl, and LiBr. The decreased solubility of both reactants by such salts facilitates their reaction to form the activated complex and thus enhances reactivity [16]. The observed decreases in the reactivity of nphali, nhi and bsali complexes hydrolysis with increasing concentration of the hydrophilic salts agrees with the anionic natureof the reactants in the rate determining step and confirms the suggested mechanism. The presence of salt decreases the solubility of the hydrophilic activated complex in the rate determining step.

The increase in the rate constant of base hydrolysis of the investigated comlexes at lower concentrations of TMTB, TETB and TBAB is explained by the anionic nature of the transition state step in our proposed reaction pathway. The subsequent decrease in the reactivity by higher concentration of TMTB, TETB and TBAB can be attributed to the dominating desolvation effect of the hydrophobic cations on OH^- ions (hydrophilic) by its characteristic hydrophobic hydration and the extensive solvation of the less hydrophobic of the investigated complexes. Again TMTB, TETB and TBAB, in low concentrations, forms linear quadrupole B^{2-} Bu_4N^+ OH^- Na^+ by the nucleophilic catalysis of the charge separation that expands the voids of hydrogen-bonded H_2O molecules.

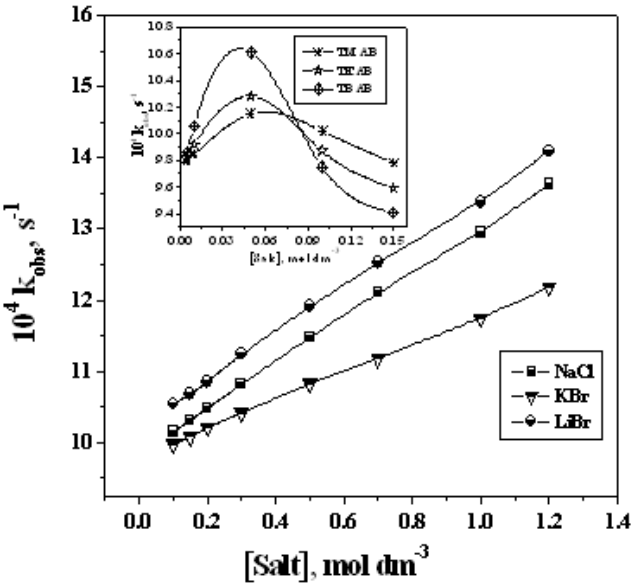


Fig. (1): Dependence of k_{obs} for the base hydrolysis of nali complex on the concentration of the added salts at [nali] = 1 × 10^{-4} mol dm^{-3}, [OH^-] = 5.83 × 10^{-3} mol dm^{-3} and 298 K.

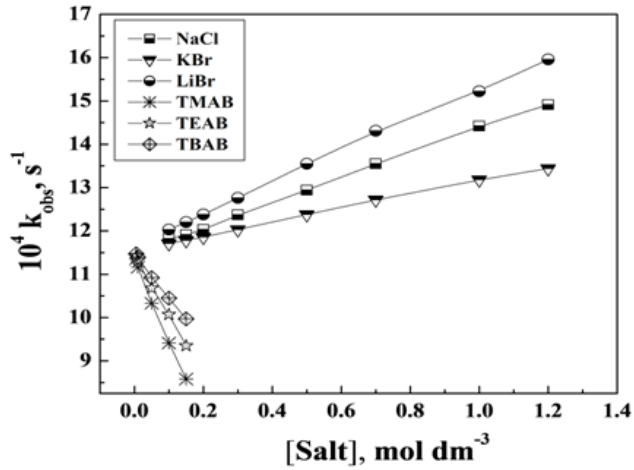


Fig. (2): Dependence of k_{obs} for the base hydrolysis of nphali complex on the concentration of the added salts at [nphali] = 1 × 10^{-4} mol dm^{-3}, [OH^-] = 5.83 × 10^{-3} mol dm^{-3} and 298 K.

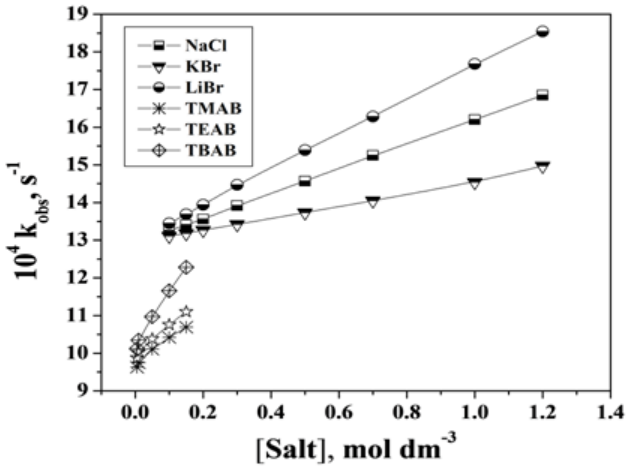


Fig. (3): Dependence of k_{obs} for the base hydrolysis of nasi complex on the concentration of the added salts at [nasi] = 1 × 10^{-4} mol dm^{-3}, [OH^-] = 5.83 × 10^{-3} mol dm^{-3} and 298 K.

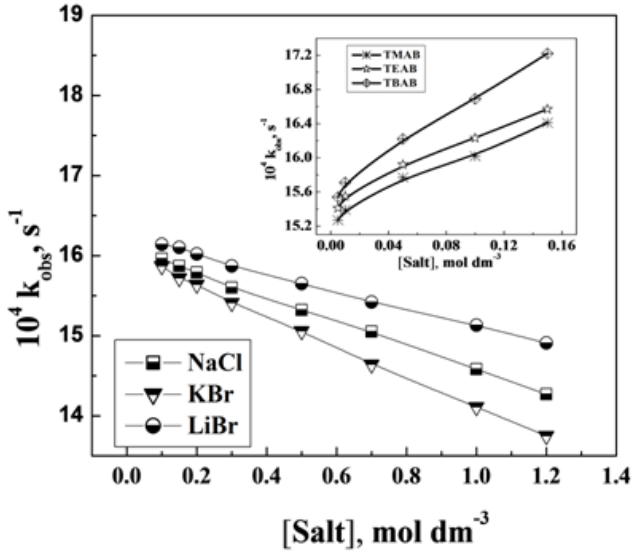


Fig. (4): Dependence of k_{obs} for the base hydrolysis of nhi complex on the concentration of the added salts at [nhi] = 1 × 10^{-4} mol dm^{-3}, [OH^-] = 5.83 × 10^{-3} mol dm^{-3} and 298 K.

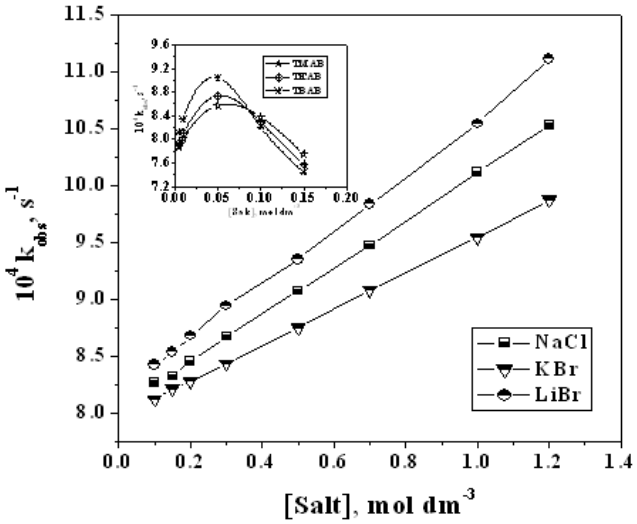


Fig. (5): Dependence of k_{obs} for the base hydrolysis of nari complex on the concentration of the added salts at [nari] = 1×10^{-4} mol dm^{-3}, [OH^-] = 5.83×10^{-3} mol dm^{-3} and 298 K

4. Conclusion

As a general trend concerning salt effects on different substrates is that as the hydrophobicity of the complex or ligand increases the relative effects of alkali metal and tetra alkly ammonium salt decreases. The highly electrostriction alkali metal halides vice, LiBr, KBr, NaCl, etc. as salting out reagents result in a more compact binding of the hydrophobic organic reactants with each other so that the activated complex is formed easily and hence the reactions proceed faster. On the other hand, tetra–n-butyl ammonium bromide (TBAB) as a salting in reagent increase the solvation of the organic reactants so much that they tend to exist separately and thus the formation of the activated complex become difficult. But in the case of our investigated base hydrolysis of the inorganic Fe(II) Schiff base amino acid complexes, the salting in effect of (TBAB) enhanced the OH^- ion attack, and hence the formation of the activated complex becomes more attainable and the reaction faster.

Acknowledgements

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