



ORIGINAL ARTICLE

# Hydrophobicity, reactivity trends of base catalyzed hydrolysis of some novel high spin Fe(II) Schiff base amino acid chelates in some binary aqueous solvent mixtures: Initial-transition state analysis



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## KEYWORDS

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Initial state-transition state

**Abstract** Rate constants for the base hydrolysis of bis(naphthylidene alanate)iron(II) (nali), bis(naphthylidene phenylalanate)iron(II) (nphali), bis(naphthylidene aspartate)iron(II) (nasi), (naphthylidene histidinate)iron(II) (nhi), bis(naphthylidene arginate)iron(II) (nari) have been reported in different binary aqueous solvent mixtures at 298 K. The observed reactivity trends are discussed in terms of the hydrophilic and hydrophobic forms of the complexes investigated, as well as the transfer chemical potentials of the hydroxide ion and the complex. Both the solvent–solute and solvent–solvent interactions have been considered. The hydrophobic character of the complexes studied was manifested by a decrease in reactivity. Solvent effect on reactivity trends of the investigated complexes have been analyzed into initial and transition state components. This can be achieved by using the transfer chemical potentials of the reactants and the kinetic data of the studied compounds. The decrease in the observed rate constant values ( $k_{\text{obs}}$ ) of the base hydrolysis of the investigated complexes with increase of solvent% is dominated by the initial state (IS).

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## 1. Introduction

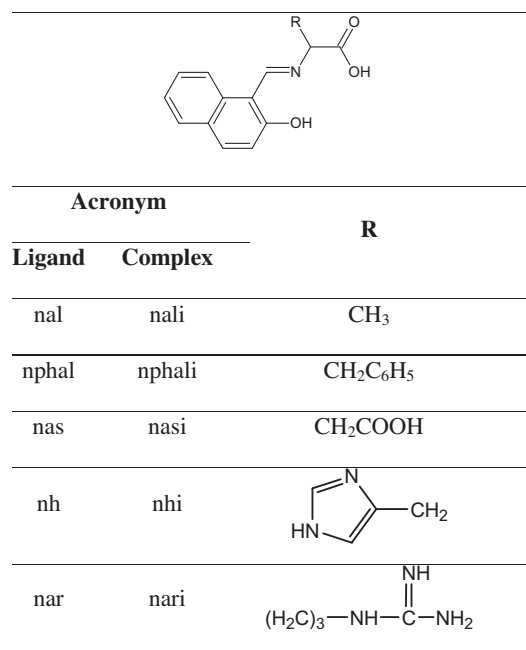
Schiff base amino acid complexes act as good chelating agents [1–3] and behave as efficient biologically active [4–5] and cytotoxic [6] agents. In addition, Schiff base amino acids complexes are considered to constitute new kinds of potential antibacterial and anticancer reagents [3,4,7,8].

The effects of both solvents upon a variety of reactions of transition metal complexes have been of interest in recent years. Most reactions of inorganic complexes exhibit different reactivities in micellar and microemulsion systems from those in aqueous solutions. Thus, the appropriate use of microemulsions can allow kinetic studies to be made of reactions involving either water-insoluble reactants or, in some cases, such Schiff base amino acid complexes, hydrophobic substrates [9,10]. More recently, trends in transfer chemical potentials and their relation to reactivity trends for substitution and redox reactions of these inorganic complexes have been investigated in binary aqueous mixtures [11]. Furthermore, a new approach to understanding solvent effects on reaction rates involves consideration of the extent of the interaction of the solvent environments of the initial state and the transition state with the solvent co sphere of an added substance [12]. Most treatments of solvent effects on reactivity deal with the rate constant and activation parameter trends, but others have recognized that such kinetic parameters are of composite values. Analysis of solvent effects on reactivities in terms of the contributions from the initial and transition states can lead to full explanations of these trends [9,10,13]. In parallel with these trends, solvation effects can be probed via the variation of activation volume with the properties of the solvent [14]. These two approaches are complementary in that analysis of the initial and transition states provides information on solvation changes for a reaction involved in a suggested mechanism on transfer from one medium to another, whereas knowledge of the activation volume can test solvation changes on going from the initial to the transition state in a specific medium [15,16]. It is worthy to recall that thermodynamic functions, e.g., solubility, provides information on transfer of the initial state, whereas solvent effects on the transition state can be derived from these measurements and the observed rate constants [14]. In the present contribution, we present an extensive investigation of these approaches through the study of solvent effects on the reactivity of the base hydrolysis of a new series of hydrophobic high-spin iron(II) amino acid Schiff base chelates. Our study aims to study the extent of the stability of the investigated complexes in different media which may be included in industry.

## 2. Experimental

### 2.1. Preparation of the investigated complexes

The solid Schiff base amino acid Fe(II) complexes were prepared by mixing aqueous solutions of the respective amino acids [L-alanine (ala), L-phenylalanine (phala), L-aspartic acid (asp), L-histidine (his) and L-arginine (arg)] with an equimolar hot ethanolic solution of 2-hydroxy-1-naphthaldehyde (HN). The resulting Schiff base amino acid ligands (the ligands are displayed and labeled in Scheme 1) were then treated with an aqueous solution of ferrous ammonium sulfate in an equimolar ratio. In order to avoid the oxidation of Fe(II) and the formation of Fe(OH)<sub>3</sub>, a few drops of glacial acetic acid were added [3,4,17]. The resulting solution was stirred for 8 h under nitrogen. The precipitated complexes were filtered off, washed with a water-ethanol mixture, and then with diethyl ether. The complexes were first dried on a water bath and then in vacuo over P<sub>2</sub>O<sub>5</sub>. The isolated complexes were crystallized from



**Scheme 1** Structures and abbreviations of the Schiff base ligands and abbreviations of their corresponding complexes.

water-ethanol solutions [3,4]. The composition of the complexes was established by CHN microanalysis, IR, and UV/vis spectral analyses. All gave satisfactory CHN microanalysis [3,4]. The stability of solutions was tested for at least a month for evidence of oxidation of the Fe(II) cation by peroxopersulfate or reduction by dithionite. When the aged complex solutions were treated with NaOH under nitrogen, a green precipitate of Fe(OH)<sub>2</sub> formed, indicating the maintenance of Fe(II) oxidation state in the complex solutions used in the kinetic runs. It was observed that, in these runs, the intensely violet color of the complex fades and the solution turns colorless. Some green colloidal particles of Fe(OH)<sub>2</sub> form initially, turning pale yellow, and, finally, precipitating as brown Fe(OH)<sub>3</sub> by oxidation with O<sub>2</sub> dissolved in solution kept long after the end of the kinetic run. Full details of the characterization of the present complexes can be found in our previous publication [3,4]. The purity of the prepared complexes was checked by their visible spectrum [3,4].

### 2.2. Kinetics

Kinetic measurements were carried out spectrophotometrically by following the decrease in absorbance with time at  $\lambda_{\max}$  in the UV-vis region appropriate to each complex. The kinetic data were recorded using in PG UV-Visible spectrophotometer model T + 80 with 10 mm matched quartz cells connected with an ultrathermostate (CRIOTERM model 190) water circulator. The reactants were brought together so that the reaction exhibits pseudo-first order kinetics by mixing a multifold greater concentration of the base than that of the complex. It was confirmed that there is no interference from other reagents at the selected wavelength absorption maxima for the investigated complexes. Rate constants were calculated from the dependence of absorbance on time at  $\lambda_{\max}$  for the base hydro-

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