

On the mechanism of indium(III) complex formation with metallochromic indicators

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ABSTRACT

The equilibria and kinetics of the interaction of In(III) with Alizarin Red S (ALZS) and Methyl Thymol Blue (MTB) dyes in aqueous solution were investigated. Spectrophotometric titrations at different pHs (1.8–2.7 range) revealed that, concerning the In-ALZS system, under conditions of metal excess the prevailing complex is ML, while stopped flow experiments have shown that, in the investigated pH range the kinetics are monophasic although the ML complex is formed through different paths involving both $\text{In}(\text{H}_2\text{O})_6^{3+}$ and $\text{In}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ as active species reacting with the monoprotonated ligand (HL). The In-MTB system was studied with the same methodology in the pH range 1.0–2.0. The complex (MH_3L) prevails although the above metal species react with differently protonated forms of the ligand. The In-MTB system displays a biphasic kinetic behavior involving a network of reaction steps, where fast pre-equilibria related to metal coordination at the carboxylates/nitrogen site, precedes slow coordination at the phenol/phenol or phenol/quinone sites. The key role in the reaction mechanism is played by the ligand features rather than by the solvent/ligand substitution process.

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1. Introduction

Tervalent metal ions of the group 13 have attracted, in recent years, growing interest since the discovery that they can be employed in a variety of applications of biological and/or medical interest [1]. Moreover, in laboratory procedures they can profitably replace methods that are slowly being phased out in an attempt of progressively moving towards mild and facile reactions belonging to the so called “green chemistry” [2–6]. In this kind of chemistry, water is mainly used as the reaction medium and metals are

supplied bound to suitable ligands. The resulting complexes should be stable enough to prevent hydrolysis and precipitation of the metal, but not so stable to hinder the action of the metal on the chemical processes involving the metal itself, as, for instance, metal catalysed reactions [7–9] or metal transfer to biological carriers [10–12]. Also, metal complexes of metallochromic indicators are encountering renewed interest due to possible application in frontier research, for instance such as new materials for dosimeters in radiotherapy [13,14].

In our studies on the thermodynamic and kinetic aspects of the coordination chemistry of aluminium, gallium, and indium complexes [15–25], we have been exploring the binding of In(III) with a variety of ligands including Transferrin, the main scavenger for trivalent metal ions in the body [10]. Actually, the investigated complexes can display interesting opportunities for the use of these metals in the etiology and diagnosis of disease because of their great mobility and relatively low toxicity [26–28].

In the framework of the above cited studies, we present here an investigation of the interaction of In(III) with Alizarin Red S (ALZS) and Methyl Thymol Blue (MTB) (Fig. 1) aimed to find the thermodynamic and kinetic parameters that can serve to optimize the conditions for the above mentioned applications. Moreover, the analysis of the binding reaction features is here employed to get more light on the mechanism of ligand substitution at In(III), that

Abbreviations: ALZS, Alizarin Red S; MTB, Methyl Thymol Blue; C_M , total analytical In(III) concentration; C_L , total analytical dye concentration; M_f , L_f , free metal and ligand; ML_T , total complex; α_i , fraction of the i -th form of the free ligand/dye; β_M , fraction of the In^{3+} species of the free metal; K_{app} , apparent overall equilibrium constant; K_{A_i} , i -th acid dissociation constant of the dye; K_{C_i} , i -th acid dissociation constant of the complex; K_f , equilibrium constant for i -complex formation; K_{OH} , equilibrium constant for formation of an hydroxo-species of the metal; k_f , forward rate constant of i -th path of reaction scheme; k_{-i} , backward rate constant of i -th path of reaction scheme; K_p , apparent overall equilibrium constant for pre-equilibrium step; K_i^* , pre-equilibrium constants of the i -th kinetic path; $K_{C_i}^*$, acid dissociation constant of the i -th intermediate complex; $\Delta A = A - A_0$, being A_0 the initial absorbance; $\Delta \varepsilon = \varepsilon_{\text{product}} - \varepsilon_{\text{reactant}}$, being ε the molar extinction coefficient. Any additional detail is given in the reaction schemes provided.

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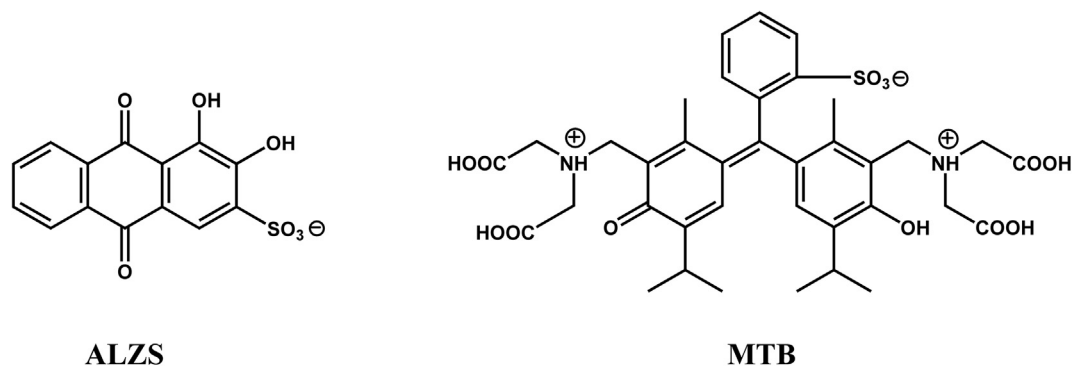


Fig. 1. Structures of the ligands: Alizarin Red S (ALZS) in the form H_2L^- , Methyl Thymol Blue (MTB) in the form H_7L^+ .

still needs to be better clarified, in spite of the relatively abundant studies devoted to this topic.

2. Experimental

2.1. Materials

All the chemicals not expressly cited are of analytical grade and were employed without further purification. Indium(III) perchlorate was prepared by dissolving a weighted amount of the pure metal in concentrated perchloric acid [10]. The In(III) concentration in the stock solutions (ca. 0.1 M) was determined by EDTA titration using PAN as an indicator [29] and resulted to be identical with that calculated from the weight of the dissolved metal. The solutions of the complexing indicators, Alizarin Red S (1,2-dihydroxyanthraquinone-3-sulphonate), here denoted as ALZS and Methyl Thymol Blue (3,3'-bis-[N,N'-di(carboxymethyl)-amino-methyl] thymolsulphophthalein), here denoted as MTB, were prepared dissolving the solid in water, kept in the dark at 4 °C and used within one week. As the indicator dyes might not be stable in solution for long time, spectrophotometric checks were made. Absorbance measurements of dye solutions, performed over at least 3 h (which is more than the time range of a spectrophotometric titration and a set of kinetic experiments), did not show any change, thus indicating that no noticeable dye decomposition occurred in this time lapse at 25 °C. Moreover, the spectra of the ligand, recorded in the cuvette at zero metal addition, were always in accordance; this result corroborates the above check ensuring that the ligand solutions are stable under the described precautions. Ultra-pure water (Sartorius) was used to prepare the solutions and as the reaction medium.

2.2. Methods

The pH measurements were made using a Metrohm 713 pH-meter equipped with a combined glass microelectrode and using a known procedure that allows the pH-meter readings to provide directly the values of $-\text{Log}[H^+]$ [30]. NaClO_4 was appropriately added in order to obtain the desired values of ionic strength.

The spectral measurements were performed using a Shimadzu 2450 double-beam spectrophotometer in quartz cells (1 cm path length) thermostatted to within ± 0.1 °C. Complex formation equilibria were investigated by adding calibrated amounts of In(ClO_4)₃ solution directly into the spectrophotometric cell containing a known volume of the ligand solution ($C_L = 2.0 \times 10^{-4}$ M for ALZS, $C_L = 5.0 \times 10^{-5}$ M or 1.0×10^{-4} M for MTB). Both solutions were brought to the same acidity and ionic strength before mixing. The experimental conditions are such that the C_M/C_L is higher than 10 for all the data points employed to evaluate the equilibria

of the 1:1 complexes. The additions were made by a Hamilton micro-syringe connected to a Mitutoyo micrometric screw; such a system enables additions of titrant solution as small as 0.164 μL . The read absorbance values were corrected for the dilution effect before analysis. The titrations were performed at different pH values, the pH range investigated being 1.8–2.7 for the In(III)-ALZS system and 1.0–2.0 for the In(III)-MTB system.

The kinetics of the complex formation reactions were investigated using the stopped-flow method. The apparatus, assembled in our laboratory, uses a Hi-Tech SHU-61SX2 sample handling unit with a mixing time of about 1 ms [31]. The kinetic experiments were all done under pseudo first-order conditions, keeping the analytical concentration of metal ion, C_M , at least ten times higher than that of the ligand, C_L ($C_M \geq 10C_L$, for In(III)-ALZS $C_L = 1.0 \times 10^{-4}$ M, $C_M = 1.0 \times 10^{-3}$ M– 1.6×10^{-2} M and for In(III)-MTB $C_L = 1.3 \times 10^{-5}$ M, $C_M = 1.9 \times 10^{-4}$ M– 1.5×10^{-2} M). Both solutions were brought to the same acidity and ionic strength before mixing and the absorbance change describing the reaction course was monitored spectrophotometrically at $\lambda = 530$ nm in the case of the In-ALZS system and $\lambda = 560$ nm in the case of the In-MTB system. At least five kinetic traces were obtained for each sample, the maximum spread of the relevant time constant being 10%. The traces were collected by a Tektronix 2210 digital storage oscilloscope and then transferred to a personal computer where they were accumulated and processed according to single or double exponential functions. The kinetic experiments were performed at different pH values, the pH range investigated being 2.0–2.7 for the In(III)-ALZS system and 1.0–2.0 for the In(III)-MTB system.

Both the static and the kinetic experiments were analysed using a non-linear least square program of the Jandel Scientific package (AISN software, Richmond, CA) which makes use of the Marquardt algorithm [32]. The In(III)-MTB system was analysed also using the program Mathematica (Wolfram Research).

3. Results – the In(III)-ALZS system

The acid dissociation constants of ALZS are $\text{p}K_{\text{SO}_3\text{H}} < 1$, $\text{p}K_{\text{A}1} = 5.54$ and $\text{p}K_{\text{A}2} = 11.01$ [33]. These values indicate that, in the range of pH explored in the present study ($1.8 < \text{pH} < 2.7$), the ligand is present essentially in its diprotonated form (H_2L^-). Fig. S1 of the Supporting Information shows the spectra of ALZS and of a mixture of ALZS and In(ClO_4)₃, both recorded at $\text{pH} = 2.7$. Since the metal is present in excess, the complex formed presents essentially a 1:1 stoichiometry, as indicated by the well-defined isobestic point generated during a titration (inset). At constant pH, the complex formation process can be represented by the apparent reaction (1)



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