



Solvation structures in zirconium-amide interaction processes: A Raman spectroscopic study



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ABSTRACT

Zr(IV)-protic amide interactions in solution were investigated for the first time by Raman spectroscopy. The dependence of the ZrCl₄ concentration on the spectra of formamide (FA) and *N*-methylformamide (NMF) is evaluated and upshifts are observed for the $\nu_{\text{C=O}}$ and $\nu_{\text{C-N}}$ modes. These shifts are consistent with the stabilization of a neutral amide form, in which the O and N atoms can be employed in the coordination to the metal ion. Indeed, Zr(IV)-O and Zr(IV)-N vibrations were identified in the spectra. The carbonyl stretching region was used for the quantitative treatment and reveals that Zr(IV) is surrounded by 4 FA molecules, in a square prismatic arrangement, while 3 NMF molecules are around the metal in an equilibrium between octahedral and square prismatic geometries, where the counter-ion also takes part in the inner-sphere.

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1. Introduction

Studies on metal complexes that are able to promote cleavage of the polypeptide backbone under non-denaturing conditions of temperature and pH have continuously increased in recent years. Cleavage takes place by either a hydrolytic or an oxidative pathway and often requires precomplexation of the metal with the polypeptide. Among numerous metals Zr(IV) has attracted special attention because it is capable of avoiding undesirable side reactions that contribute to oxidative peptide cleavage [1]. Furthermore, some authors have correlated the +4 oxidation state to its preference for the oxygen atom so that the formation of hydrolytically inactive peptide amide nitrogen complexes could be avoided [2–5]. In spite of these advantages, some discrepancies on the catalytic activity of this metal ion are still found in the literature. For instance, Komiyama and coworkers [6] have reported that Zr(IV) catalyzed only very low levels of peptide hydrolysis in tris(hydroxymethyl) aminomethane buffer pH 7.0. On the other hand, Kassai et al. [7] observed that 4,13-diaza-18-crown-6 substantially increases the rate of Zr(IV)-assisted peptide hydrolysis at neutral pH. However, insoluble compounds were formed in all reactions and such finding led those authors to speculate that Zr(IV)-assisted peptide hydrolysis might have a

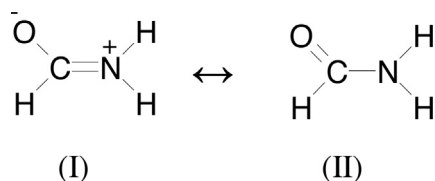
heterogeneous component similar to that exhibited by lanthanide hydroxide gels [6].

Zr(IV) hydrolysis in aqueous solutions has been mainly investigated by small-angle X-ray scattering (SAXS) and extended X-ray absorption fine structure (EXAFS) [8,9]. Tetramer units, which form larger polynuclear complexes in the course of ageing, aggregate to eventually produce gels or precipitates. So far, it has been well established that eight oxygen atoms are coordinated to a zirconium atom in aqueous medium. However, the formation of different metal–amide, metal–water and metal–hydroxide complexes as well as heterogeneous solutions make hard the elucidation of the precise mechanism through which Zr(IV) catalyzes peptide hydrolysis.

Our laboratory is interested in using vibrational spectroscopy to predict the catalytic activity of some metals toward amide hydrolysis reactions [10–15]. Initially, metal–amide interactions have been studied in order to account for the activation of the carbonyl group before the nucleophilic attack (water or hydroxide). The results show that the spectral pattern for divalent transition metal ions, such as Zn, Ni, Cu and Fe is always the same. That is, the $\nu_{\text{C=O}}$ vibration is downshifted whereas the $\nu_{\text{C=N}}$ mode of the amide is upshifted, enabling the stabilization of a dipolar amide structure (I), which is considered the active species for catalysis. In contrast, the upshifts observed for both $\nu_{\text{C=O}}$ and $\nu_{\text{C=N}}$ modes, in the presence of Al and Fe(III), indicate that a neutral amide form (II), hydrolytically inactive, is stabilized by these ions.

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In this paper, we present a Raman spectroscopic study on the interaction of a Zr(IV) salt with two selected protic amides. Such investigation will allow a more reliable structural analysis since the competition with aqua and hydroxo ligands can be avoided. The shifts observed at the ν_{CO} and ν_{CN} regions will be useful for evaluating if either a dipolar (I) or neutral (II) amide structure will be stabilized. Considering that the stabilization of each one seems to be dependent on the charge density of the ions, the high positive value of Zr(IV) will be then essential for the present study. The average number of amide molecules in the inner-sphere of the metal ion will be also determined and correlated to information obtained at the region characteristic of the Zr(IV)-ligand vibrations.

2. Methodology

2.1. Reactants and sample preparations

All chemicals were purchased from Sigma–Aldrich. Formamide (FA) and *N*-methylformamide (NMF) were distilled under reduced pressure, discarding the first and last portions of distillate. ZrCl_4 was used without any additional purification. Since the chemicals are sensitive to moisture, they were handled in a controlled N_2 atmosphere dry-box. Solutions were prepared by weight, and all concentrations are expressed as molalities (mol kg^{-1}).

2.2. Instrumental details and data analysis

Raman spectra were recorded on a SENTERRA dispersive Raman microscope, equipped with a thermoelectrically-cooled CCD detector and a long working-length objective (20 \times lens). The 532 nm line of a diode laser was used as Raman excitation source in 180 $^\circ$ scattering geometry and the acquisition time for each spectrum was 60 s per window. The solutions were inserted in NMR tubes and the spectra were obtained at the temperature of 20 ± 2 $^\circ\text{C}$, by using 4 cm^{-1} spectral resolution and laser power equal to 20 mW.

The curve-fitting analyses were done using OMNIC 7.3 software, which is suited for determining multiple components under the experimental envelope. The individual components are very well

supported by analogy with the pure solvent spectrum with regard to the number, half height band widths, relative positions and intensities. Each component, which has been considered as a Voigt function, was fitted by a systematic series of band parameters until contours in spectra of several different solutions were matched by changing only the height of the components. The results also showed excellent agreement with those obtained from the second derivatives of the original spectra.

3. Results and discussion

Raman spectra of pure liquid FA and its solutions containing variable amounts of ZrCl_4 are shown in Fig. 1. As the salt concentration increases from 0.1 to 1.0 molal, a new band arises in the 1770–1635 cm^{-1} range. It is exactly located at 1746 cm^{-1} and has its intensity enhanced at the expense of the asymmetric FA band. Additional information can be obtained in the region between 1425 and 1260 cm^{-1} , where the original FA bands at 1390 ($\delta_{\text{C-H}}$) and 1310 cm^{-1} ($\nu_{\text{C-N}}$) are now accompanied by two others at 1378 and 1353 cm^{-1} . A downshift of approximately 12 cm^{-1} is observed and has been commonly reported for the $\delta_{\text{C-H}}$ vibration of coordinated FA [10–15]. Besides it, one can observe that the $\nu_{\text{C=O}}$ and $\nu_{\text{C-N}}$ modes of FA are upshifted upon coordination to Zr(IV). These shifts indicate that a neutral FA form (II) is stabilized and it is also important to stress that such structure contains both O and N atoms as likely active sites. Clearfield and Malkiewicz [16] synthesized amide complexes with ZrCl_4 and their IR spectra were examined. The downshift of $\nu_{\text{C=O}}$ and the upshift of the $\nu_{\text{C=N}}$ vibration were observed for coordinated *N,N*-dimethylformamide (DMF), indicating a bonding to the metal through the O atom. On the other hand, the $\nu_{\text{C=O}}$ mode of the FA complex was upshifted and led the workers to assume that non-coordinated FA molecules were held in the structure by H-bonds. Since X-ray measurements have not been used, structural conclusion was not achieved for the complexes. However, the upshift of the $\nu_{\text{C=O}}$ mode observed for the FA complex is in line with our finding in solution.

NMF is also a good model to describe the peptide bond, but the presence of the alkyl group could cause some orientation change toward the metal ion. As can be seen in Fig. 2, upshifts are also observed for NMF solutions with different quantities of the Zr(IV) salt. At the $\nu_{\text{C=O}}$ region, which comprises the 1780–1610 cm^{-1} range, a new band at 1754 cm^{-1} is present in the spectra and its intensity increases with increasing salt concentration. Nevertheless, it is much smaller than that exhibited by the 1746 cm^{-1} band of the FA complex (Fig. 1). Actually, another band at around 1700 cm^{-1} seems to be present in the asymmetric band envelope of NMF and details on this region will be further presented. Concerning the range between 1320 and 1200 cm^{-1} , usually

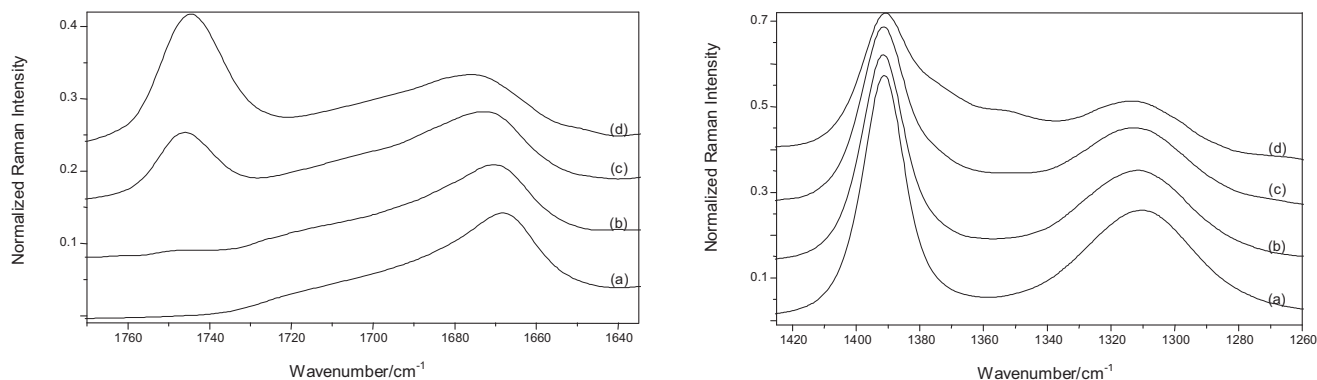


Fig. 1. Raman spectra of pure liquid FA and in the presence of ZrCl_4 for the $\nu_{\text{C=O}}$ (left panel) and $\delta_{\text{C-H}}$ and $\nu_{\text{C-N}}$ regions (right panel). Molal concentrations (mol kg^{-1}): (a) solvent; (b) 0.1; (c) 0.5; (d) 1.0.

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