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Raman and NMR kinetics study of the formation of amidoamines containing N-hydroxyethyl groups and investigations on their Cu(II) complexes in water

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ABSTRACT

Three amidoamines containing the N-hydroxyethyl group (^{HO}Et), namely (^{HO}Et)$_2$N(CH$_2$)$_2$C(O)NH$_2$ (**1**), [(^{HO}Et)$_2$N(CH$_2$)$_2$C(O)NH]$_2$CH$_2$ (**2**) and ^{HO}EtN[(CH$_2$)$_2$C(O)NH$_2$]$_2$ (**3**) have been synthesized by reacting diethanolamine ^{HO}Et$_2$NH with acrylamide and *N,N′*-methylenebisacrylamide (respectively **1** and **2**) and ethanolamine ^{HO}EtNH$_2$ with acrylamide (**3**). Four other compounds corresponding to **1** and **2**, but derived from *sec*-amines Me$_2$NH (**4** and **5**) and Et$_2$NH (**6** and **7**) have been prepared for the sake of comparison of the spectroscopic features. All compounds have been obtained by the well-known aza-Michael addition between an N-nucleophile and an activated vinyl group.

The reaction in water between diethanolamine and acrylamide leading to **1** has been monitored in situ by Raman and NMR spectroscopy, both techniques confirming second order kinetics and giving values for kinetic constants in excellent agreement. The coordination ability of **1** and **2** towards Cu^{2+} in water has been studied by the Job's plot method. Spectroscopic data indicate that ligand **1** prevalently forms a 4:1 Ligand/Metal complex with a (N,O$_3$) coordination set on the equatorial plane of Cu^{2+}, whereas ligand **2**, containing two amide functionalities bridged by a methylene group, appears able to form a 1:1 Ligand/Metal chelate species, again with a (N,O$_3$) donor set around copper.

1. Introduction

Amidoamines are β-amino carbonyl compounds obtained by the so-called aza-Michael addition, a simple reaction between nitrogen nucleophiles (usually amines) and activated electrophilic olefins (usually acrylamides) [1–7].

The β-amino carbonyl compounds are versatile intermediate molecules for the synthesis of nitrogen-containing products, such as antibiotics, β-amino alcohols, optically active amino acids, products with a wide range of biological activities or pharmacological properties [8–11].

The Michael reaction is carried out very efficiently in polar solvents, at room temperature, enabling the preparation of a wide range of molecules and without or with catalyst, usually either acidic or basic [12–15]. Significant rate acceleration of this reaction is observed in water, compared to organic solvents [16–18]: this is explained by H-bonding of H$_2$O to the amine and carbonyl groups of α,β-unsaturated compounds [14,17].

A typical example of aza-Michael reaction is the addition of a *sec*-amine to an acrylamide, illustrated in Scheme 1, where R$_1$ is an alkyl group and R$_2$ is H or an alkyl group.

Due to mild and green reaction conditions and absence of volatile or dangerous byproducts, the Michael addition is a versatile synthetic method for applications in emerging technologies, allowing the design of a wide range of tailored macromolecular architectures [19], ranging from linear thermoplastic to hyperbranched and crosslinked polymers [20–24].

An important class of polymers obtained by aza-Michael reaction are the poly(amidoamine)s (PAAs) synthesized by reaction of *prim*-amines or *sec*-diamines with bisacrylamides, according to Schemes 2 and 3, where R, R$_{1–3}$ are aliphatic radicals.

Almost all conceivable bisacrylamides and *prim*- or *sec*-amines can be employed as monomers, giving PAAs of nearly unique structural versatility among polymers obtained by stepwise polyaddition. PAAs are *by themselves* functional polymers, but, by further functionalization, as

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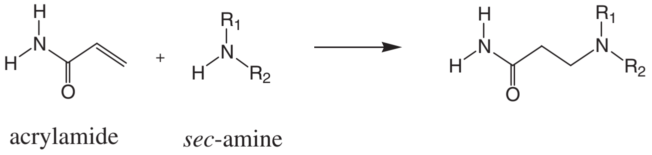


Scheme 1. Amidoamine by Michael addition.

suggested by Ferruti [25], versatile polymeric structures may be obtained for several environmental, pharmaceutical and medical applications [26–30].

In this regard, if the nucleophilic amines bear functional groups, they can provide PAAs with further reactivity. In particular, the presence of a hydroxyl group in the starting amine (e.g. R_1 = hydroxyethyl group ^{HO}Et in Scheme 2) could increase water solubility, H-bond networking ability and metal coordination power of the resulting polymer [31,32]. Furthermore, it is worth noticing that the hydroxyl functions produce strong interactions with lignocellulosic materials through hydrogen bonds, promoting effective anchoring to wood and paper artifacts [33, 34]. This gives to the PAAs de-acidifying and biocidal properties, which can be enhanced by the presence of borate groups or metal cations, such as Cu^{2+}, grafted to the polymers [35–37].

Regarding metal cations, Ferruti and coworkers [38] found that coordination complexes with transition metal ions are formed by PAAs in free-linear, cross-linked and silica-grafted forms. Moreover, the same group aimed attention at characterizing copper(II) complexes of PAAs by means of potentiometric and spectroscopic techniques (UV-VIS absorption and ESR) [38–41]. Non-macromolecular models of the polymers were also studied, discovering that their corresponding copper(II) complexes show electronic and ESR spectra identical to those observed for the PAAs complexes and suggesting the possible formation of CuN_2O_4 chromophores [39].

Here we report about the synthesis, the characterization by ESI-MS, FTIR, Raman, NMR techniques and the study of ligand behavior of amidoamines, containing the N-hydroxyethyl group (^{HO}Et), towards Cu^{2+} cations in water solution. These molecules can be considered models of the PAAs containing alcoholic dangling groups and therefore these investigations give insight into the coordination ability of PAAs, which are effectively used for the protection of lignocellulosic materials even in addition with copper(II) salts. In particular, this paper deals with kinetic studies of the reaction between diethanolamine and acrylamide in water by means of Raman and NMR spectroscopy. Whereas NMR is a well consolidated tool for kinetic studies in organic and organometallic chemistry, Raman spectroscopy is scarcely applied in this field, although it has been shown to be particularly useful for in situ monitoring of organic syntheses in aqueous solution [42–45], requiring no sample preparation.

2. Experiment

2.1. Materials and data collection

N,N′-Methylenebisacrylamide (hereafter called MBA) (99%), acrylamide (hereafter called AA) (98%), diethylamine (99.5%), ethanolamine (98%), diethanolamine (99.5%), dimethylamine (water solution 45%), copper chloride (99%), copper sulfate (99%) were purchased from Sigma-Aldrich: all were used as received.

C, H, N elemental analyses were carried out by using a Carlo Erba EA1108 microanalyzer. Electrospray ionization mass spectrometry (ESI-MS) was recorded using Thermo Scientific™ LTQ XL Linear Ion Trap Mass Spectrometer (Ion spray voltage 4 kV, capillary temperature, 200 °C; sheath gas flow rate 5 (arb.)). Samples were solubilized in methanol. Flow injection analysis was done in positive ionization mode and in full scan mode across the 50.00–250.00 *m*/*z* range.

NMR spectra were acquired with Bruker AVANCE 300 and Bruker AVANCE 400 NMR spectrometers. The instruments use a 5 mm multinuclear probe (^{1}H, ^{13}C), for high resolution with actively shielded gradient along the z-axis, equipped for automatic tuning and matching. The samples were dissolved in deuterated solvents: D_2O, DMSO-d_6, $CDCl_3$.

Fourier-Transform Infrared (FT-IR) spectra were collected with a Bruker Equinox 55 spectrometer equipped with a Golden Gate (Specac) ATR diamond accessory. The spectral resolution was 4 cm^{-1}, operating in the 4.000–400 cm^{-1} range. Data were elaborated with OPUS software.

Non-polarized Raman spectra on the samples were recorded at 632.8 nm and 473.1 nm in a nearly backscattered geometry with a Horiba - Jobin Yvon LabRam micro-spectrometer (300 mm focal length) equipped with an integrated Olympus BX40 microscope. The spectral resolution was about 1.5 cm^{-1}. The Rayleigh radiation was blocked by an edge filter and the backscattered Raman light was dispersed by an 1800 grooves/mm holographic grating on a Peltier cooled CCD, consisting of an array of 1024 × 256 pixels. The entrance slit width was fixed at 100 μm. The laser power on the samples was adjusted by means of density filters to avoid uncontrolled thermal effects and was always kept less than 1 mW. Spectra were collected using a long working distance ×50 microscope objective. Typical exposures were 10–20 s, with 3–5 repetitions. The system was regularly calibrated using the 520.6 cm^{-1} Raman band of silicon. The data analysis was performed by LABSPEC 5.78.24, Jobin Yvon Horiba, built-in software package.

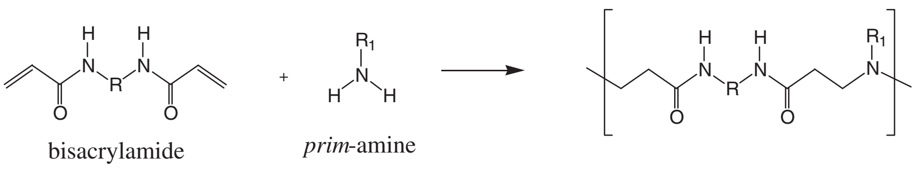
The UV–vis absorption spectra were collected using a Thermo Evolution 260 Bio spectrophotometer provided with a Peltier thermostating device, and quartz cuvettes (1 cm path length).

2.2. Synthesis of aza-Michael adducts

2.2.1. $(^{HO}Et)_2N(CH_2)_2C(O)NH_2$ 3-[bis(2-hydroxyethyl)amino]propanamide **(entry 1)** [46]

A water solution of diethanolamine (0.68 ml, 7.03 mmol) was added to a water solution of acrylamide (0.5 g, 7.03 mmol). The reaction mixture was stirred at room temperature for 4 h and then the solvent was evaporated in vacuo to give the crude product (yield: 99%) as a pale yellow viscous liquid.

IR (ATR): 2949, 2875, 1667, 1610, 1405, 1273, 1144, 1025, 904, 874, 573 cm^{-1}; Raman: 2951, 2924, 2887, 2837, 1668, 1614, 1412, 1375, 1140, 1113, 1022, 991, 906, 872, 806 cm^{-1}; δ_H (400 MHz DMSO): 7.53 (1H, br s, N$\underline{H}_2$), 6.87 (1H, br s, N$\underline{H}_2$), 4.31 (2H, br s, $NCH_2CH_2O\underline{H}$), 3.47 (4H, t, *J* 6.3 Hz, $NCH_2C\underline{H}_2OH$), 2.74 (2H, t, *J* 6.9 Hz, $NC\underline{H}_2CH_2CO$), 2.56 (4H, t, *J* 6.3 Hz, $NC\underline{H}_2CH_2OH$), 2.23 (2H, t, *J* 6.9 Hz, $NCH_2C\underline{H}_2CO$); δ_C (100.6 MHz, DMSO): 174.71, 59.56, 56.51, 50.98, 33.49; *m*/*z* (ESI-MS): 177.22, $C_7H_{16}N_2O_3$ requires 176.19; Anal. Calcd. for $C_7H_{16}N_2O_3$: C, 47.72; H, 9.15; N, 15.90%. Found: C, 46.98; H, 9.21; N, 15.81%.



Scheme 2. Polyamidoamine by Micheal addition.