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An experimental and theoretical vibrational study of interaction of adenine and thymine with artificial seawaters: A prebiotic chemistry experiment

Pedro R. Anizelli [a], João P.T. Baú [a], Henrique S. Nabeshima [b], Marcello F. da Costa [b], Henrique de Santana [a], Dimas A.M. Zaia [a,*]

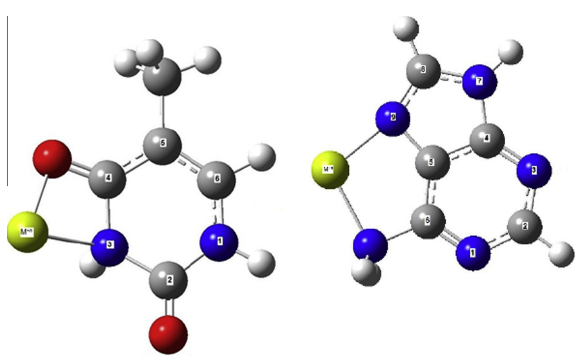
[a] Laboratório de Química Prebiótica, Departamento de Química-CCE, Universidade Estadual de Londrina, 86051-990 Londrina, PR, Brazil
[b] Departamento de Física-CCE, Universidade Estadual de Londrina, 86051-990 Londrina, PR, Brazil

HIGHLIGHTS

- Interaction nucleic acid bases/seawater is an important issue for prebiotic chemistry.
- Several elements of seawater play important roles in the living beings.
- Sr^{2+} interacts with thymine, thus it could be important for the prebiotic chemistry.
- Adenine interacts with all cations of artificial seawaters.

GRAPHICAL ABSTRACT

(a) Interaction of metal with thymine. (b) Interaction of metal with adenine.



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ABSTRACT

Nucleic acid bases play important roles in living beings. Thus, their interaction with salts the prebiotic Earth could be an important issue for the understanding of origin of life. In this study, the effect of pH and artificial seawaters on the structure of adenine and thymine was studied via parallel determinations using FT-IR, Raman spectroscopy and theoretical calculations. Thymine and adenine lyophilized in solutions at basic and acidic conditions showed characteristic bands of the enol-imino tautomer due to the deprotonation and the hydrochloride form due to protonation, respectively. The interaction of thymine and adenine with different seawaters representative of different geological periods on Earth was also studied. In the case of thymine a strong interaction with Sr^{2+} promoted changes in the Raman and infrared spectra. For adenine changes in infrared and Raman spectra were observed in the presence of salts from all seawaters tested. The experimental results were compared to theoretical calculations, which showed structural changes due to the presence of ions Na^{+}, Mg^{2+}, Ca^{2+} and Sr^{2+} of artificial seawaters. For thymine the bands arising from $C_4{=}C_5$ and $C_6{=}O$ stretching were shifted to lower values, and for adenine, a new band at 1310 cm^{-1} was observed. The reactivity of adenine and thymine was studied by comparing changes in nucleophilicity and energy of the HOMO orbital.

* Corresponding author. Tel.: +55 43 3371 4366; fax: +55 43 3371 4286.
E-mail address: damzaia@uel.br (D.A.M. Zaia).

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Introduction

The vibrational modes of nucleic acid bases play an important role in the study of the adsorption of DNA and RNA onto minerals [1], which have been examined via the use of Raman and infrared spectroscopy [2–4]. Because vibrational modes are sensitive to changes in molecular structure, these techniques can also be used to investigate conformational changes [5–7], functional changes that occur in tautomeric equilibrium [8,9] and the effect of acidic or basic groups on molecular structure [10].

The vibrational modes of adenine and thymine have previously been reported [10–14]; however, interpretations of some vibrational bands, especially in the region from 1000 to 400 cm^{-1} are controversial. Calculations have been used to assign vibrational bands detected via Raman and infrared spectroscopy, but error may arise due to the incorrect parameterization of characteristics such as hydrogen bonding, vibrational coupling and oligomerization of nitrogenous bases, which can lead to shifts of the peaks in the spectra [15–19].

Salts likely played important roles in living beings. Some divalent cations such as Ca^{2+}, Mg^{2+} and Fe^{2+} present in the prebiotic ocean precipitate some amphiphilic molecules. Divalent cations could also hydrolyze active monomers that participate in the synthesis of biopolymers [20]. Magnesium has important roles in living beings, such as stabilizing of proteins, nucleic acid bases and cell membranes by binding to the surface of these molecules. Since Mg^{2+} is part of the chlorophyll, thus its contribution to photosynthesis it is perhaps the most important function of it [21]. This cation could also catalyze the reaction of formation of nucleosides, which may have been important in RNA and DNA synthesis [22].

In most of the experiments of prebiotic chemistry, nucleic acid bases were dissolved in distilled water or sodium chloride solutions [23]. Thus, the effects of ions that may have existed in prebiotic seas have not been assessed. Additionally, the range of pH used in this study can be found in hydrothermal vents, which were also present in prebiotic seas [24]. It should also be noted that the soils of Mars have high concentrations of $MgSO_4$, NaCl and $MgCl_2$ [25], and the artificial seawaters used in this work also has a high concentration of these salts [23].

In the present study, Raman and FT-IR spectroscopy were employed to investigate the effect of pH and artificial seawater composition of different geological periods on Earth on the vibrational modes of adenine and thymine (Fig. 1). Parallel, theoretical calculations were also used to predict the molecular interactions between seawater ions and these nucleic acid bases.

Materials and methods

All the reagents were of the analytical grade P.A.

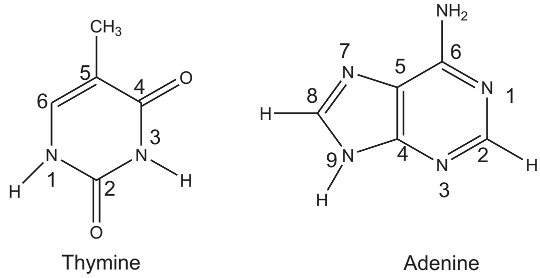

Fig. 1. Molecular structures of nucleic acid bases studied in this work.

Materials

Adenine and thymine were purchased from Sigma–Aldrich and Acros, respectively and used as received (Fig. 1).

Artificial seawater

Four different recipes of artificial seawater were prepared as described by Zaia [23].

Dissolution of adenine or thymine in distilled water

For each nucleic acid base (1000 μg mL^{-1}), 50 mL the following solutions were prepared: distilled water, acidic solution (adenine, pH 2.00; thymine, pH 0.50) and basic solution (adenine, pH 10.0; thymine, pH 11.5). All solutions were prepared using ultra pure water (MilliQ). The pH of the solutions were adjusted using HCl (0.10 mol L^{-1}) and NaOH (0.10 mol L^{-1}) no additional buffer was added. The solutions were frozen at −20 °C, after vials were connected to pump lyophilizer (high vacuum, 200 μmmHg). The solid material was then analyzed using FT-IR spectroscopy and Raman spectroscopy. Lyophilization was the preferred method to remove water because it is less aggressive than heating the sample and the structure of the products formed in solution is maintained. The chosen pH range should be representative of hydrothermal vent systems, which could range from 2.0 to 13.0 [24].

Dissolution of adenine or thymine in artificial seawater

Adenine or thymine (720 μg mL^{-1}) was dissolved in 50 mL of the following artificial seawaters: artificial seawater 0 Ga, artificial seawater 4.0 Ga, artificial hydrothermal seawater 3.20 Ga and artificial seawater 3.20 Ga. All solutions were prepared using ultra pure water (MilliQ). The solutions were lyophilized and the solids were analyzed using FT-IR spectroscopy and Raman spectroscopy as above.

Methods

Computational details

All structures were fully optimized and the frequencies were calculated for the B3LYP functional set [26–28], aug-cc-pVDZ basis set [29] and 3-21G [30] basis set for metals (Na^{+}, Mg^{2+}, Ca^{2+} and Sr^{2+}) using the Gaussian03 program [31]. The aug-cc-pVDZ basis set was chosen for the correct description of oxygen and nitrogen atoms. This basis set includes additional diffuse functions (prefix aug-), which were used to account for the relatively diffuse nature of the lone pairs. The solvent effect was calculated using the polarization model continuum (PCM) [32].

FT-IR spectroscopy

FT-IR spectra of the samples from 700 to 4000 cm^{-1} were obtained using an FT-IR (Perkin–Elmer frontier), with attenuated total reflectance (ATR). A resolution of 2 cm^{-1} and 10 scans were used to obtain the spectra. FTIR spectra were analyzed using the Origin program (8.0, 2007).

Raman spectroscopy

Raman spectra were obtained from solid samples with a micro-Raman spectrograph (DeltaNu Advantage) with a 532 nm laser line and 4 cm^{-1} resolution. Raman spectra were analyzed using the Origin program (8.0, 2007).