



Solid adenine and seawater salts exposed to gamma radiation: An FT-IR and EPR spectroscopy analysis for prebiotic chemistry

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ABSTRACT

Solids of adenine obtained from distilled water and seawater lyophilized solutions were γ irradiated at a 94.52 kGy dose. Results indicate that pure solid adenine had a low degradation rate, likewise the solid containing seawater salts. However, EPR spectroscopy analysis suggests a high interaction of the radiation with seawater salts, by radical formation in sulfate ions. These outcomes are of interest for prebiotic chemistry, since ions could have played important roles in chemical evolution. In addition, Martian soil is rich in sulphate salts, thus these salts could protected organic molecules being degraded by γ -radiation.

1. Introduction

Prebiotic Chemistry is a field in Astrobiology, which investigate the origins of life on Earth, from chemical (geochemical) to biological systems. The reactivity and decomposition of biomolecules such as amino acids, nucleic acid bases and sugars (building blocks of life) are one of the main aims on Prebiotic Chemistry [1]. The emergence of life probably occurred with the participation of these biomolecules. Thus, experiments focusing on these molecules should be carried out in accordance with Primitive Earth conditions [2].

It is known that at the early Earth, environmental ionizing radiation was more intense than nowadays [3]. This source of energy could initiate a variety of chemical reactions, including decomposition and polymerization. Zaia [2] suggested an artificial seawater to be used in Prebiotic Chemistry experiments that better resembles saline concentration of the primitive seas at 4.0 billion years ago. It should be noted that most radiolysis experiments were performed in distilled water or sodium chloride solutions or salt solutions. The artificial seawater suggested by Zaia [2] has high Mg^{2+} and SO_4^{2-} concentrations unlike the current seawater that has a higher Na^+ and Cl^- concentrations [4]. In addition, the interaction between salts of artificial seawater [2] and nucleic acid bases change their reactivity [5, 6]. The effects of ionizing radiation on

seawater decomposition, and the effect of ions on the radiolysis products of water has been reported recently [7, 8, 9]. These reports demonstrated that ionizing radiation can interact with different ions, changing the yields of water radiolysis products. The γ -irradiation of seawater promoted the formation of H_2 , O_2 and H_2O_2 [7, 8, 9]. The Br^- and Cl^- anions enhanced the formation of H_2 because, they inhibit the reaction of hydrogen with hydroxyl radical [7, 8, 9].

This work aims to understand the interactions promoted by γ radiation on solid samples of adenine obtained from both distilled water and seawater solution, resembling conditions from 4.0 billion years ago. The samples were analyzed with infrared (FT-IR) and electron paramagnetic resonance (EPR) spectroscopy.

2. Experimental

2.1. Samples preparation and cleaning of the glassware

Solid dry samples were obtained from solutions of adenine at 500 $\mu g \cdot mL^{-1}$ (in distilled water and seawater solution). The solutions were frozen in a refrigerator and further place to a pump lyophilizer (high vacuum, 50 mPa, $-50^\circ C$). The 4.0 Ga seawater solution was prepared according to Zaia [2], by the dissolution in 1.0 L of purified water

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(MilliQ) the following salts: Na_2SO_4 (0.271 g), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (0.500 g), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (2.50 g), KBr (0.050 g), K_2SO_4 (0.400 g), MgSO_4 (15.00 g).

All the glassware was cleaned according to the chemical radiation procedures. It was immersed in a hot mixture of HNO_3 and H_2SO_4 for four hours, followed by rinsing of with bidistilled water and MilliQ purified water in this order. The glassware was evolved in aluminum foil and heated at 300 °C overnight, ensuring the elimination of all organic matter.

2.2. Radiolysis

The samples were irradiated in a γ ray source (Gammabeam 651-PT, located at Institute of Nuclear Sciences, UNAM) at room temperature (298 K). The irradiation dose was determined using a ferrous sulfate-copper sulfate dosimeter. The dose rate was 197 Gy min^{-1} . Irradiation dose was 94.52 kGy.

2.3. Infrared spectroscopy (FT-IR)

The FT-IR spectra were obtained with a reflectance accessory (PerkinElmer spectrum 400, USA) in a spectrometer (PerkinElmer spectrum 400, USA). The spectra were recorded at transmittance mode from 4000 cm^{-1} –650 cm^{-1} and a resolution of 4 cm^{-1} over 10 scans.

2.4. Electron paramagnetic resonance spectroscopy (EPR)

The samples were submitted to EPR spectrometer (Jeol JES-TE300) from Chemistry Institute, UNAM, operating at X-band, with a 100 kHz modulation frequency and a cylindrical cavity in the mode TE011. The magnetic field received external calibration with a precision gaussmeter, Jeol ES-FC5. The samples were placed in a flat-type quartz cell and measured at room temperature.

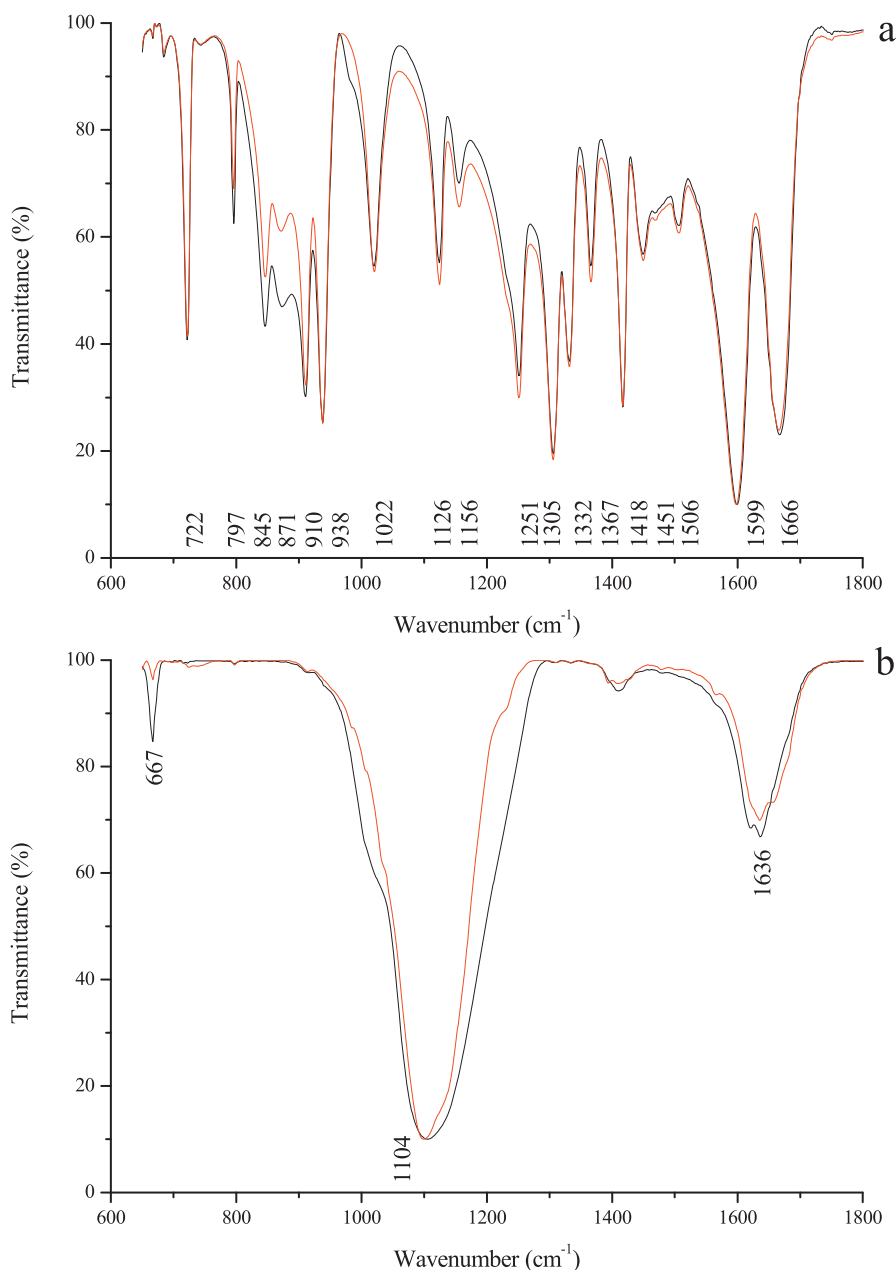


Fig. 1. FT-IR spectra of the solid of adenine obtained from the lyophilization of the adenine solution (500 $\mu\text{g} \cdot \text{mL}^{-1}$) in: a) distilled water and; b) seawater solution (4.0 Ga). Control sample (black line) and irradiated sample at 94.52 kGy (red line).

3. Results

Solid powder samples were obtained from the lyophilization of adenine solutions at $500 \mu\text{g mL}^{-1}$ (distilled water and seawater solution). These solids were γ irradiated at a dose of 94.52 kGy. No changes (shift nor new bands formation) were observed in the FT-IR spectra of the solids obtained from distilled water solution (Fig. 1-a), which suggest a low or none decomposition of adenine. The same irradiation procedure was performed on the solid obtained from seawater solution. In this last case, no bands of adenine were observed, due to the minor concentration of adenine, compared to the salts of seawater (Fig. 1-b). In the case of the sample containing adenine and seawater salts, the FT-IR spectra show

three bands at 667, 1104 and 1636 cm^{-1} . The high intense band at 1104 cm^{-1} is due to the vibrational modes ν_1 of the sulfate (SO_4^{2-}) species [10]. The third band at 1636 cm^{-1} is attributed to the bending β (H-O-H), from the hydration of the salts [11]. The control sample (without irradiation) shows a band at 667 cm^{-1} , which could be related to the sulfate bending $\beta(\text{SO}_4^{2-})$, due to formation of calcium sulfate (CaSO_4). The gypsum mineral has the same vibration frequency at the FT-IR spectra [12], as sulfate calcium salt does [13]. Nevertheless, after γ -irradiation, this frequency was observed to decrease in intensity. These results suggest an interaction of the γ radiation with the salts present in the seawater, and not merely the interaction with adenine molecule.

Moreover, the irradiation of sulfate promotes the formation of other

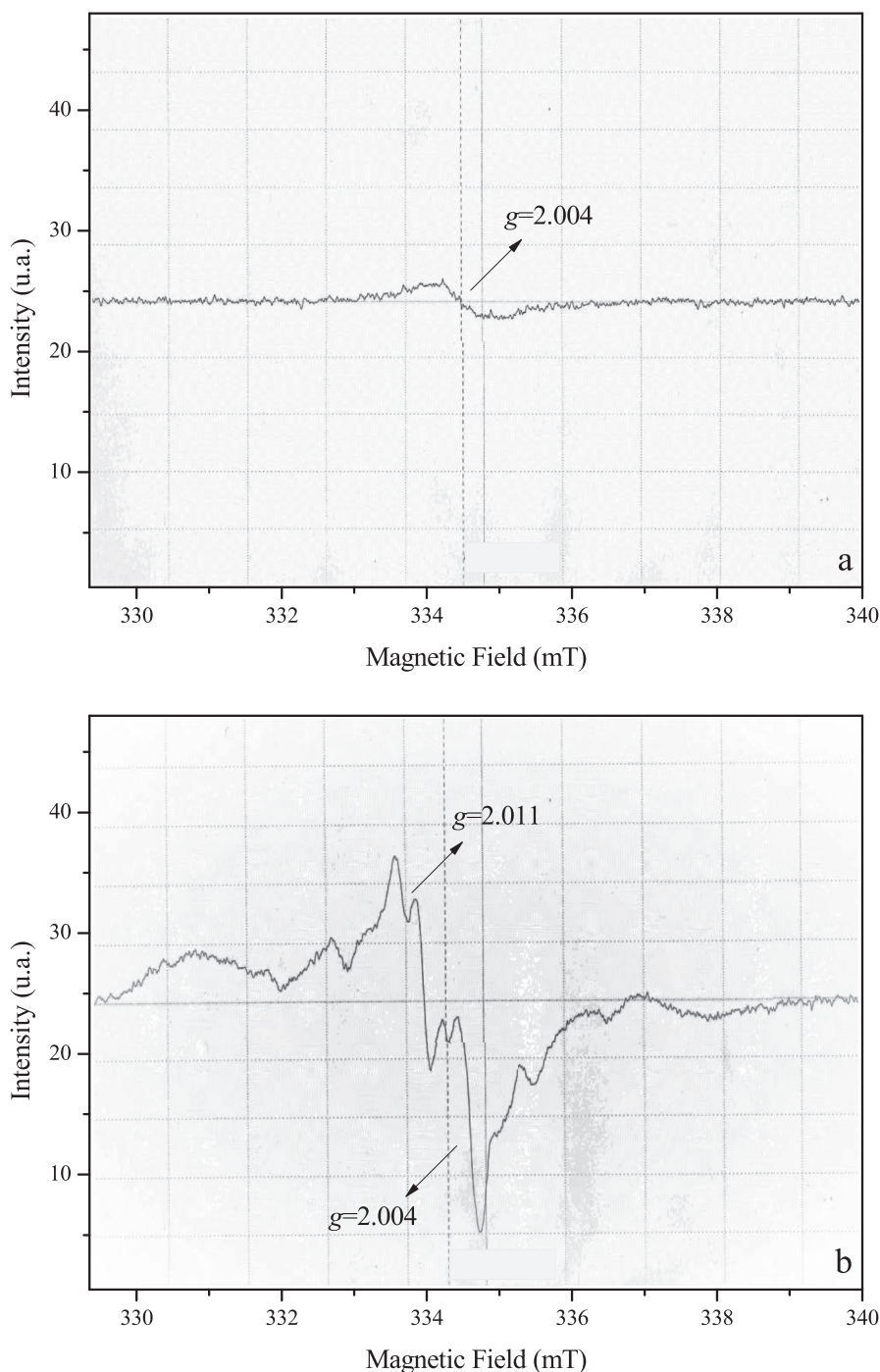


Fig. 2. EPR spectra of the solid obtained from lyophilization of the solution of: a) adenine ($500 \mu\text{g mL}^{-1}$) in: distilled water solution and irradiated at 94.52 kGy and; b) seawater solution and irradiated at 94.52 kGy.

species like SO_4^- , SO_3^- , SO_2^- , O^- and O_3^- by the formation of electron-hole trapping centers [14], being SO_4^- the primary defect produced (Eq. (1)), which may be monitored by EPR spectroscopy [15, 16].



Solid samples obtained from the lyophilization of adenine in distilled water and seawater solution were both analyzed by EPR spectroscopy before and after γ irradiation. Samples before irradiation showed no EPR signals. Whereas, irradiated samples showed EPR lines which represent the formation of free radicals induced by the γ -radiation (Fig. 2).

The EPR of the solid obtained from distilled water solution showed a resonance with $g = 2.004$, which is characteristic of free radical. This radical is very likely prominent of degradation of adenine [17]. Zehner et al. [18], describes the formation of radicals in adenine derivatives through X-rays irradiation, by the addition of a proton at carbon C₂ or C₈. The EPR of the solid obtained from seawater solution shows a much more intricate spectrum. There are several resonance lines in the spectrum and some of them are superimposed, which makes their identification difficult. This occurs because of the mixture of salts (cations and anions) in the sample.

The amount of each species at the sample of adenine plus seawater solution is described at Table 1. It should be noticed that the salt with minor concentration is the potassium bromide (KBr). Thus, the amount of the ions and adenine is related to one species (or mol) of a bromide ion (Br^-). The main species at this sample are the ions SO_4^{2-} , Cl^- , Mg^{2+} and Ca^{2+} .

After irradiation, sulfates (both the Na_2SO_4 and K_2SO_4) could generate free radicals, which are detected by EPR. Some species, such as SO_3^- in different environments could show different g values, as described in literature [19], this species generates even more probability of superimposed lines. The formation of this type of radical is well documented in the literature by EPR, including in other compounds like BaSO_4 [20, 21].

4. Discussion

In the spectrum of adenine plus seawater solution, the resonance at $g = 2.004$ is very likely due to SO_3^- . Among the radicals that could be formed after irradiation, SO_3^- appears in literature as the more intense, showing an isotropic spectroscopic factor of $g = 2.0037$ [22] and $g = 2.0033$ [15] for K_2SO_4 and $g = 2.004$ for Na_2SO_4 [23]. Although this radical shows the same g value as the radical of the solid obtained from distilled water solution, this does not necessarily means that it is the same radical. The difference in g would appear in a measure with greater precision.

Another species probably present is the SO_4^- radical. However, this radical was very difficult to identify in our spectrum since it generates several resonance lines, and its intensity is much weaker than the one from SO_3^- [22]. Unlike SO_3^- , the SO_4^- radical is anisotropic, showing three g values [22, 23]. The SO_4^- can occupy two non-equivalent sites when

present in K_2SO_4 structure, [22]. In this case, instead three g values, we would recommend six. Another consideration, for Na_2SO_4 , is the possibility of hyperfine interaction with 3/2 nucleus [23]. All these resonance lines are probably superimposed in our spectrum.

The SO_3^- radical, as in the case of SO_4^- , shows an anisotropic g , both in K_2SO_4 and in CaSO_4 [22, 23]. However, it was very difficult the identification, because of the salt mixture.

Lastly, although the mixture of salts has several resonance lines, it is possible to identify the $g = 2.011$ as probably due to O_3^- . This radical appears in literature as an isotropic g value resonance, showing $g = 2.0116$ for K_2SO_4 structure [22] and 2.0100 for Na_2SO_4 [23]. It should be noticed that some lines in the spectrum could be due to hyperfine interaction from others nucleus spin configuration. Nevertheless, FT-IR points out to modifications on the sulfate species.

In terms of prebiotic chemistry, the interactions of biomolecules with ions from seawater salts could give a clue on Chemical Evolution processes. Cations from seawater can decrease the free energy of nucleic acid bases, such as adenine [5]. The results here discussed points out some remarks. Firstly, in solid state, some reactivity of the γ -irradiated adenine is observed. Second, in seawater solution due to the salts, it is possible that a minor amount of adenine molecules interacts with the γ radiation; this effect could have diminishing the decomposition of organic molecules.

It should be pointed out that Mars's surface has a high concentration of sulfate salts [24, 25, 26]. Thus, organic matter might be preserved by the mechanism here described. These sulfates present in Martian soils would interact with ionizing radiation that reaches surface of Mars.

5. Conclusion

At solid state, the γ -irradiation of pure adenine promotes the formation of free radicals, detected by EPR spectroscopy, followed by small decomposition. Nevertheless, for the mixture of solid adenine and several salts from seawater, a minor interaction of γ radiation with adenine is observed, due to the effects with seawater ions detected. In order to a fully comprehension of the phenomena, some experiments including one or two sulfates species could be helpful.

The results hereby presented highlight the relevance of one scenario in prebiotic chemistry: the environments with wet/dry cycles, like tidal ponds. At the dry period, none or a very small amount of water is present. Thus, the presence of small organic species should be favored in a saline medium, since salts (ions) may have decreased the interaction with radiation effects.

Declarations

Author contribution statement

João Paulo T. Baú: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Daniel F. Valezi, Dimas A. M. Zaia, Eduardo D. Mauro: Analyzed and interpreted the data; Wrote the paper.

Sául A. Villafañe-Barajas: Performed the experiments.

María Colín-García, Alicia Negrón-Mendoza: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Table 1

Amount of each species at the sample containing adenine plus seawater salts.

Specie	n
Na^+	9.1
K^+	11.9
Mg^{2+}	302.5
Ca^{2+}	40.5
SO_4^{2-}	306.6
Cl^-	92.7
Br^-	1.0
Adenine	8.8

The amount of Br^- in mol was taken as 1.0.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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