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MICROWAVE POWER SATURATION AND DENSITY FUNCTIONAL THEORY ON IDENTIFICATION OF THE FREE RADICAL PRODUCED BY IONIZING RADIATION

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Introduction: L-asparagine dosimeter presents a complex Electron Spin Resonance (ESR) signal, with several overlapping lines, and microwave power saturation pattern. The microwave power saturation of this material reveals two values of maxima . This behavior could be associated to the formation of one or more radiation induced free radical with different relaxation times, giving different relaxation values. In this context, we combined the techniques ESR and Density Functional Theory (DFT) to analyze the possibility of formation of more than one free radical induced by ionizing radiation in the L-asparagine molecule, and how these radicals influence the spectrum and dependence on microwave power saturation

Material and method: L-asparagine (99%) obtained from Acros Chemical Company was irradiated with a 160kV/10mA X-ray source (Isovolt Titan E-160M-2 GE) with 2 mm aluminum and 0.8 mm beryllium filtration to a dose of 50Gy. ESR measurements were performed with a JEOL X-band spectrometer, model JES-FA 200 (9.5 GHz) to investigate the spectroscopic parameters. The microwave power was applied in the range of 0.1 up to 10 mW. The free radicals for L-asparagine were predicted through density functional theory (DFT) calculations using the ORCA program package. Geometry optimizations and frequency calculations of all structures were performed using the B3LYP density functional and the def2-SVP basis set. With the thermodynamical results obtained, the bond energies for the two amines and carboxyl group were calculated.

Results: The saturation curve of L-asparagine exhibits two peaks at 1.73 mW, and 3.16 mW. These two saturation values suggest the presence of more than one free radical with different relaxation times. The DFT calculation was performed by breaking the bond of both amine groups side of molecular structure (C_2 and C_4) and the carboxyl group (C_1) to understand the nature of ESR spectra of L-asparagine at room temperature. The binding energy of the amines and carboxyl group are 101.73 (C_2), 78.86 (C_4) and 110.88 (C_1) kcal mol^{-1} respectively. Therefore, the data reveals that the binding energy of the hydroxyl is higher, so it is probable that the break of both amine groups will occur. The break into C_2 is associated to the radical I and C_4 to radical II. The interaction among these radicals (I and II) with the hydrogen nucleus neighboring results in at least 8 hyperfine lines, although not completely resolved in the X-band spectrometer due to overlapping lines. The experimental and simulated spectra shows a good agreement.

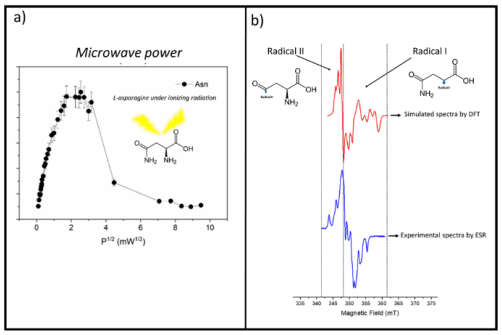

Figure 1. ESR signal intensity as function of the square root of the microwave power (a) spectra of experimental and simulated spectra (b).

Conclusions: The complex ESR spectra of L-asparagine could be associated to more than one free radical. The DFT shows the possible free radicals induced by ionizing radiation at room temperature considering the binding energy of the groups, and considering the higher probability of the formation to radical I and II associated to amine group. These radicals have several overlapping lines with different values of power saturation. Thefore, the combination of the two tecniques were able to describe qualitatively and quantitatively of the nature of free radical inducend in L-asparagine dosimeter.

References:

1. Iara S. Lima, Guidelli E.J and Baffa O. *Potential properties of L-Asparagine for ESR dosimetry applications*, Radiation Physics and Chemistry 180, 109204 (2020).

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