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The effect of Hg(II) ions on the free radicals of humic substances and their model compounds.

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Streszczenie

Humic acids (HAs) and humin (HU) complexes with Hg(II) ions were studied using EPR, FTIR and CP MAS (13)C NMR spectroscopies. The analysis of the EPR spectra showed, especially for HA, a significant decrease in the g-factor value for the resulting Hg(II) radical species, as compared with that observed for the parent radicals. The concentration of the formed radical complexes was very low, precluding their detailed characterization. For this reason hydroxybenzenes and their benzoic acids were used as models of the humic substances' radical centres able to form radical ligands towards Hg(II) ions. The resulting radicals, characterized by a g-factor lower than that of the free electron (2.0006-2.00017), were efficiently produced upon Hg(II) complexation only for the hydroxybenzenes with their OH groups in the ortho position and, what is more important, the presence of carboxylic substituents was not necessary. It is most likely that formation of the radicals characterised by low g-factor proceeded in two steps. The first is oxidation process of the hydroxybenzenes and their derivatives resulting in a typical phenolic/semiquinone type radical while in the second step the radical is complexed by the excess of Hg(II), as the result spin density of the radical is shifted towards aromatic ring leading to the observed lowering of the g parameter value. The redox character of the process starting from Hg(II) was confirmed by the formation of elemental mercury. The g-factor of the semiquinone radical obtained from 2,4,6-trihydroxybenzoic acid was not changed by Hg(II) ions coordination, as indicated by g =2.0034.

Słowa kluczowe

humic substances, Semiquinone radicals, HG(II), EPR spectroscopy

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