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Original scientific paper

EPR study of the production of OH radicals in aqueous solutions of uranium irradiated by ultraviolet light

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Abstract: The aim of the study was to establish whether hydroxyl radicals ($\bullet\text{OH}$) were produced in UV-irradiated aqueous solutions of uranyl salts. The production of $\bullet\text{OH}$ was studied in uranyl acetate and nitrate solutions by an EPR spin trap method over a wide pH range, with variation of the uranium concentrations. The production of $\bullet\text{OH}$ in uranyl solutions irradiated with UV was unequivocally demonstrated for the first time using the EPR spin-trapping method. The production of $\bullet\text{OH}$ can be connected to speciation of uranium species in aqueous solutions, showing a complex dependence on the solution pH. When compared with the results of radiative de-excitation of excited uranyl ($^*\text{UO}_2^{2+}$) by the quenching of its fluorescence, the present results indicate that the generation of hydroxyl radicals plays a major role in the fluorescence decay of $^*\text{UO}_2^{2+}$. The role of the presence of carbonates and counter ions pertinent to environmental conditions in biological systems on the production of hydroxyl radicals was also assessed in an attempt to reveal the mechanism of $^*\text{UO}_2^{2+}$ de-excitation. Various mechanisms, including $\bullet\text{OH}$ production, are inferred but the main point is that the generation of $\bullet\text{OH}$ in uranium containing solutions must be considered when assessing uranium toxicity.

Keywords: uranium fluorescence; OH radicals; electron paramagnetic resonance; spin trap; DEPMPO.

INTRODUCTION

The uranyl ion and its luminescence have been the subject of intensive research for more than a 100 years.¹ There are several monographs and a large number of papers dealing with various aspects of this topic, including photochemical reactions between excited uranyl ($^*\text{UO}_2^{2+}$) and both inorganic and organic compounds.^{1–6} These reactions are enabled by the fact that $^*\text{UO}_2^{2+}$ has a high oxidative potential ($E^\ominus(^*\text{UO}_2^{2+}/\text{UO}_2^{2+}) = 2.6 \text{ V}$) and can readily oxidize different substrates.⁷ During photochemical reactions, quenching of the uranyl fluorescence occurs, which is supposed to be the consequence of the pro-

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duction of non-luminescent uranium forms, such as UO_2^{2+} and U(IV) ; this phenomenon is observed even in pure water solutions of inorganic uranyl salts.⁸ Studies showed that the quenching is dependent on solution speciation, the presence of impurities, solution acidity and temperature.^{9–11} There are several proposed mechanisms for explaining this process, which can be reduced to four: auto-quenching, electron transfer, hydrolysis of excited uranyl and abstraction of hydrogen from the substrate.⁷ However, due to the complexity of uranium speciation in solution¹⁰ and the structure of the excited states of uranyl,¹² none of them can be considered as a complete description of the UO_2^{2+} fluorescence quenching process. Special interest has been shown in the photophysics and photochemistry of $^*\text{UO}_2^{2+}$ in aqueous solutions, probably because of their possible influence on the processes in the environment. In a series of papers dedicated to this problem,^{8–11} a research group from the University of Coimbra (Portugal) proposed, as the most probable mechanism of UO_2^{2+} fluorescence quenching, OH radicals ($^*\text{OH}$) produced in the process of hydrogen abstraction from water molecules. This process is thermodynamically favorable because the redox pair $^*\text{UO}_2^{2+} / \text{UO}_2^{2+}$ has a higher oxidizing potential than the $^*\text{H}\cdot\text{OH}/\text{H}_2\text{O}$ pair ($E^\ominus(^*\text{H}\cdot\text{OH}/\text{H}_2\text{O}) = 2.48 \text{ V}$).⁷ However, the production of OH radicals has only been studied at relatively high uranium concentrations and low pH (where UO_2^{2+} are the dominant species), which is not the case in the environment and biological systems. It has been shown that the hydroxyl radical exists in uranyl solutions of high acidity (pH 1 or lower) or in the presence of polymolybdates, but the origin of those radicals is uncertain.^{13–16} As a concurrent mechanism for the production of hydroxyl radicals, a reaction of water and organic radicals, previously formed in the interaction of an excited uranyl ion and a spin trap, was proposed.¹⁶

The aim of this work was to investigate the production of hydroxyl radicals in aqueous uranyl solutions irradiated by UV light, using EPR spin trap methods, in order to prove the existence of this species. To assess the influence of different forms of uranyl in solution on the production of $^*\text{OH}$, the reaction was studied over a wide pH range with varying uranium concentration and in the presence of different counter-ions. The obtained results are discussed in terms of possible pathways of hydroxyl radical generation and the influence of different excited species of uranyl.

EXPERIMENTAL

Solutions of $\text{UO}_2(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Na_2CO_3 were prepared by dissolving analytical grade chemicals (Merck, Germany) in deionized water (MiliQ). The pH values of the solutions were adjusted by adding of 0.10 M HCl and 0.10 M NaOH and controlled by a pH-meter. The spin trapping agent was DEPMPO, 5-(diethoxyphosphoryl)-5-methyl-1-pyrroline-*N*-oxide (Alexis, USA), because it can distinguish between different mechanisms of OH radical formation.¹⁷ Solutions together with the spin trap were placed in quartz cuvettes and irradiated in a self-made UV reactor at a wavelength of $300 \pm 10 \text{ nm}$ (UVB). The

wavelength of UV light was selected to be close enough to that of an excitation laser (335 nm) frequently used in uranyl fluorescence studies. It was shown¹⁸ that higher energy states of excited uranyl de-excite to the first excited state by internal conversion or non-radiative transfer to the surrounding molecules. Following irradiation, the solutions were transferred to Teflon tubes and the trapped radicals were measured using a Varian E104-A X-band EPR spectrometer (modulation amplitude: 2 G, power: 10 mW). The spectra were processed by Microcal Origin™ v. 7.5 software using window average smoothing. The intensity of the DEPMPO/OH peak in the adduct spectra was measured as the peak-to-peak height (line indicated by the arrow in Fig. 1). All experiments were performed at ambient temperature (22 °C).

Uranium shows complex behavior in aqueous solutions depending on the acidity and composition of the solution; hence it is necessary to predict the relative abundance of different uranyl species under various conditions. The theoretical calculation of their equilibrium concentrations was performed using Phreeqc v. 2.13 software (USGSC),¹⁹ for which purpose, the program uses thermodynamic equilibrium constants data. As calculation input, temperature, composition and pH value of the solution were taken. The output file of the program contains information about the concentrations of all species present in the solution or in the solid phase (see Fig. 3).

RESULTS AND DISCUSSION

The EPR spectra of the DEPMPO adduct produced by irradiation of 4.2×10^{-5} mol dm⁻³ solution of uranyl acetate, which contained DEPMPO (0.10 mol dm⁻³), at different pH values, are shown in Figs. 1b–1d. The corresponding spectra obtained for uranyl nitrate contained the same spectral lines. A typical spectrum of the DEPMPO/OH adduct is given for comparison in Fig. 1a. All the EPR spectra obtained in this study showed the presence of this adduct, which can be considered as proof for the production of OH radicals in UV irradiated solutions of uranyl ions. The blank probe, consisting only of irradiated deionized water and the spin trap, showed no EPR spectra. Also, a solution of uranyl and the spin-trap showed no EPR spectra (Fig. 1), and Fig. 1 shows that a small amount of some adducts other than DEPMPO/OH was present at higher pH values. A possible explanation for this in solutions containing CH₃COO⁻ could be the generation of an adduct with acetate radicals, formed in reaction with the excited uranyl ion. However, the existence of same lines in the spectra obtained for uranyl nitrate solutions and the fact that the formation of the acetate radicals is favored in solutions of low pH,⁷ makes this explanation less probable. On the other hand, other excited uranyl species, which are present in solutions at the intermediate pH values, could have de-excitation pathways other than ^{*}UO₂²⁺; these routes may involve the production of free radicals. One of the proposed mechanisms for quenching uranyl fluorescence involves reversible crossing between two excited states of UO₂²⁺ (U^{*} and X^{*}) and separate routes of their de-excitation^{7,9} (Fig. 2). It has been assumed that processes of non-radiative de-excitation of the X^{*} state include the generation of •OH.^{9,16} However, in the case of complex uranyl species, even the de-excitation of the U^{*} state could involve free radical production other than hydroxyl in solution (see below).

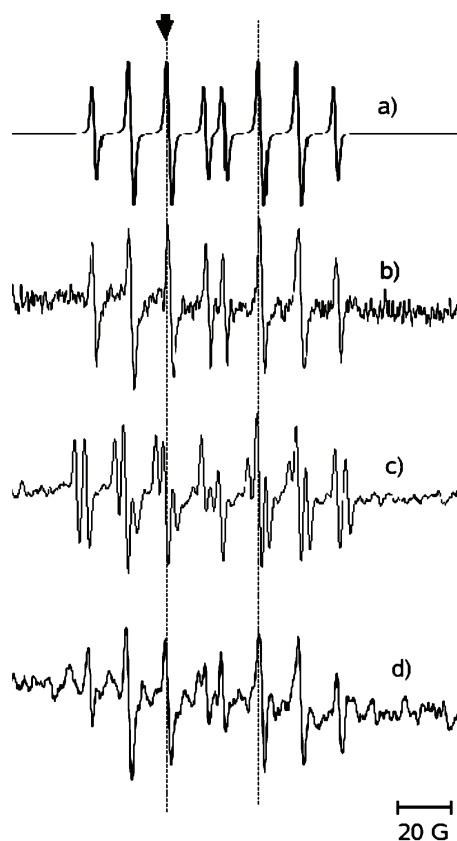


Fig. 1. EPR spectra of DEPMPO adducts: a) simulated EPR spectra of DEPMPO/OH¹⁷ and spectra obtained by UV irradiation (wavelength: 300 nm) of uranyl acetate solution (the uranium concentration was 10 ppm, the concentration of the spin trap DEPMPO was 0.1 mol dm⁻³) at different pH values: b) 2.0, c) 7.0 and d) 10.0. The arrow indicates the line which was the least affected by the presence and which was used for peak-to-peak measurements of the EPR signal height. The dashed line is used to indicate the alignment of the EPR spectra.

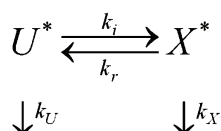


Fig. 2. The mechanism of quenching of uranyl fluorescence proposed by Formosinho,⁹ where U* is the higher excited state of the uranyl ion, X* is the first excited state of UO₂²⁺, k_i and k_r are constants of crossing between states, k_U and k_X are cumulative rate constants for the de-excitation processes.

The complexity of the EPR spectra obtained for solutions at intermediate pH somewhat complicates the quantitative assessment of DEPMPO/OH adducts; hence, for this purpose, the line which is the least affected by the presence of other adducts (indicated by arrow in Fig. 1) was selected.

It is well known that different uranyl species exist in aqueous solutions at different pH values,²⁰ which can be the explanation for the different DEPMPO adducts. The calculated distribution of uranyl species in the pure solutions used for UV irradiation is given in Fig. 3. In solutions of both uranyl acetate and uranyl nitrate at pH < 5, the most dominant specie is the free uranyl ion (with a hydration layer). Above this value, positively charged hydroxyl complexes of the uranyl ion become dominant, while at pH > 8, the only species present in the

solution is $(\text{UO}_2)_3(\text{OH})_5^+$. As shown in Fig. 3, the concentration of these species is not equal to the total uranium concentration because of the existence of a solid phase in the form of $\text{UO}_2(\text{OH})_2$ and $\text{UO}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (schoepite) in this pH range (the solid phases are not presented in the diagram). In solutions with an excess of carbonates, the hydroxyl complexes are replaced with carbonate complexes of uranyl, which are negatively charged and no solid phase is formed. It has been shown that the structure of the energetic levels of excited uranyl in complexes becomes altered in comparison to UO_2^{2+} (low pH), which in turn should have an impact on the uranyl fluorescence lifetime and spectra. Consequently, the production of OH radicals in the reaction of hydrogen abstraction¹⁶ should also be affected by uranyl speciation.

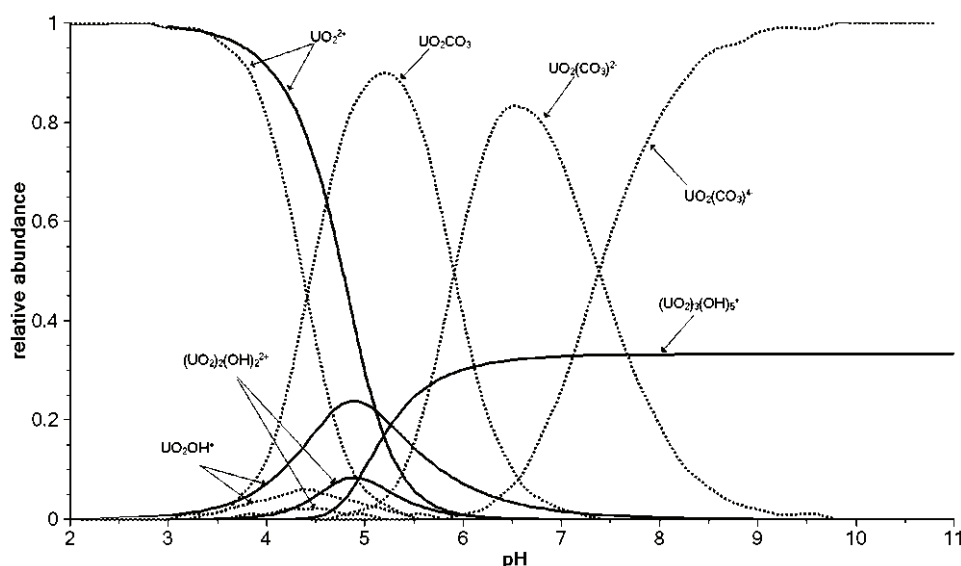


Fig. 3. Relative abundances of uranyl species in a solution of uranyl acetate: abundances in the absence (—) and in the presence (---) of carbonates.

The pH dependence of the signal height of the DEPMPO/OH adduct produced in a solution of uranyl acetate upon irradiation with UVB light is shown in Fig. 4. The pH profile of the adduct signal at $\text{pH} < 6$ qualitatively follows the concentration profile of the free uranyl ion, *i.e.*, a high and steady production of OH radicals up to $\text{pH} 4$, followed by a decline between $\text{pH} 4$ and 6 (see Fig. 3). This implies that $^*\text{UO}_2^{2+}$ plays a major role in $\cdot\text{OH}$ production in this pH range. Fomosinho *et al.*,⁹ considering uranyl fluorescence quenching in the pH range between 1 and 4, showed that the quenching constant depends on the pH of the solution, but the pH dependence of the profile showed an unexpected minimum around $\text{pH} 3$, which was explained by the presence of a strongly fluorescent hyd-

roxy complex of uranyl. Since the EPR method directly measures the production of hydroxyl radicals while the study of $^*UO_2^{2+}$ de-excitation by fluorimetry just indirectly suggests their presence, the conclusion can be drawn of the co-existence of other non-radiative decay processes.

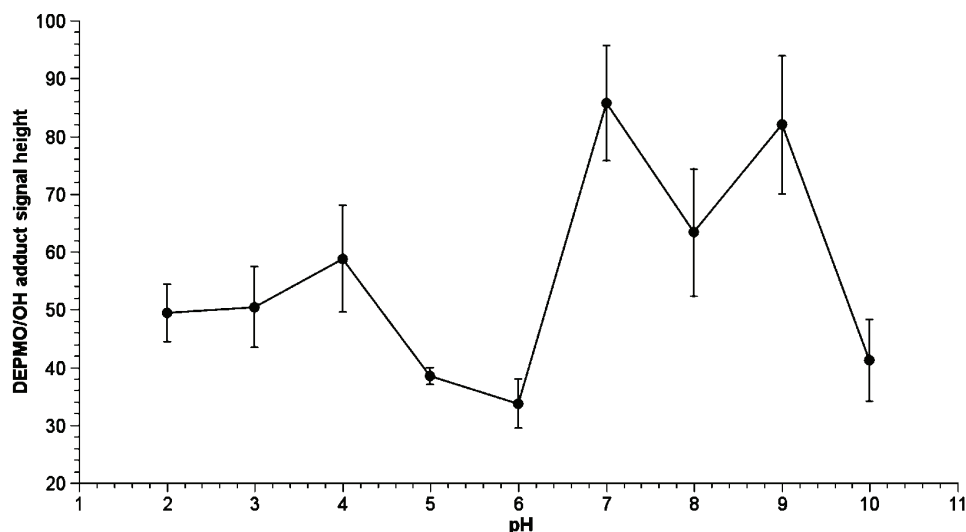


Fig. 4. pH dependence of the signal height of the DEPMPO/OH adduct produced in a solution of uranyl acetate (concentration of uranium: 10 ppm) by irradiation with UVB light.

In the pH range between 4 and 6, there is a drop in the production of OH radicals, which could be a consequence of various mechanisms. Firstly, uranium speciation in this range shows the presence of two hydroxyl complexes of uranyl ion with overlapping abundance profiles. Due to the low concentrations of these species, their impact on OH radical production should be small. However, Park *et al.*²¹ observed that the fluorescence decay of uranyl above pH 3 has two components, which arise from two excited species: $^*UO_2^{2+}$ and $^*(UO_2)_2(OH)_2^{2+}$; the fluorescence of the second species decays five times slower than the first one.²¹ The concentration profile for $(UO_2)_2(OH)_2^{2+}$ (see Fig. 3) shows that it has a small abundance in this pH region. Considering the previously mentioned facts, the conclusion can be drawn that this species has a small influence on OH radical production. Secondly, in this pH range, the EPR spectra showed, in addition to the signal of the DEPMPO/OH adduct, additional lines which probably arise from the DEPMPO adduct of an unknown radical species (see Fig. 1c), the production of which could be a concurrent process to hydroxyl radical generation. A possible explanation could be the generation of organic radicals in reactions with excited uranyl ions, which was previously found in studies of UO_2^{2+} fluorescence quenching.^{3,4} Since acetates were present in the solution, a reaction could occur

via hydrogen abstraction from C_{α} with the generation of acetate radicals. However, the fact that the additional signals also exist in solutions of uranyl nitrate in this pH range favors the assumption that $*(UO_2)_2(OH)_2^{2+}$ shows different de-excitation pathways, one involving an OH radical and the other the production of an unknown free radical.

At pH values higher than 6, the signal of the DEPMPO/OH adduct first shows an increase, a slight variation around pH 8, followed by a drop of the signal height above pH 9. The speciation diagram (see Fig. 3) shows a dominance of the polyuranyl hydroxyl complex $(UO_2)_3(OH)_5^+$ in this region, the concentration of which remains unaltered throughout the region. In comparison with the OH radical yield in the region below pH 5, OH radical production in the pH region 7–9 showed higher efficiency. This could be explained by the formation of the uranyl exciplex species, $*UO_2(UO_2)_2(OH)_5^+$ (or $*UO_2(*UO_2)_2(OH)_5^+$, which is less probable). The formation of exciplex species in a uranium solution is theoretically possible, but has not yet been experimentally confirmed,⁸ and also the Phreeqc program cannot take into account the existence of such species. It is possible that the coordinated OH^- in this species can act as some kind of mediators in the process of $\bullet OH$ formation. It is premature to speculate whether this can explain the sudden drop of $\bullet OH$ production at pH 10.

The dependencies between the DEPMPO/OH adduct signal and the concentration of uranium at pH 2 for solutions of uranyl acetate and uranyl nitrate are shown in Fig. 5. It appears that $\bullet OH$ production is almost independent of the uranium concentration for both uranyl acetate and nitrate. The data for uranyl nitrate are in agreement with the concentration independence of the fluorescence decay constant of the excited uranyl ion,^{9,21} but the authors did not give an explanation of such behavior. The same dependence was found in case of uranium acetate solutions, which may imply that the mechanism of OH radical production at pH 2 does not depend on the employed uranyl compound (acetate or nitrate). A slight increase in the DEPMPO/OH adduct signal in case of the nitrate solution was observed at higher uranium concentration. This can be explained by the following: the generation of hydroxyl radicals involves the production of UO_2^+ which is further converted to U(IV); this process is possible only in the presence of an $\bullet OH$ scavenger (hydroxyl radicals are good oxidants and can oxidize UO_2^+ back to the uranyl ion). However, if nitrates are present in a low pH solution, they can perform re-oxidation⁷ of UO_2^+ to UO_2^{2+} . It is possible that above a certain uranyl nitrate concentration, this process becomes dominant; hence more UO_2^{2+} is “recycled” and available for excitation.

The same dependence but at pH 10.0 is shown in Fig. 6. The adduct signal showed no concentration dependence below 5 ppm for uranyl nitrate solutions, after which there was a steady increase in $\bullet OH$ production. A similar situation exists for uranyl acetate solutions, except that the threshold is at 3 ppm. The pro-

duction of $\bullet\text{OH}$ was generally higher in nitrate solutions. This again indicates that different species are involved in the production of OH radicals at different pH values, but also indicates that the counter ions play a significant role at high pH values. The Phreeqc calculation showed (not included in Fig. 3) the existence of small quantities of UO_2NO_3^+ . There is thus a possibility of the formation of an excited mixed nitrate–hydroxyl complex, which could be de-excited easier by $\bullet\text{OH}$ production.

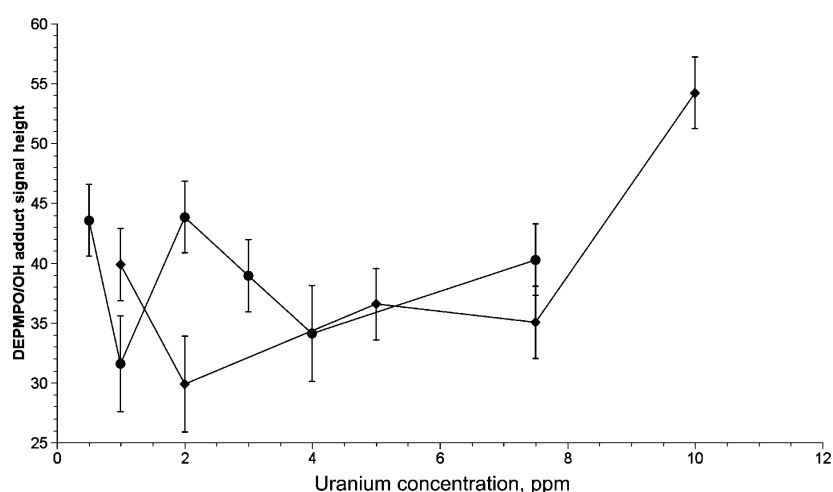


Fig. 5. Uranium concentration dependence of the signal of DEPMPO/OH, produced in solutions of uranyl acetate (●) and uranyl nitrate (◆), pH 2.0, by irradiation with UVB light.

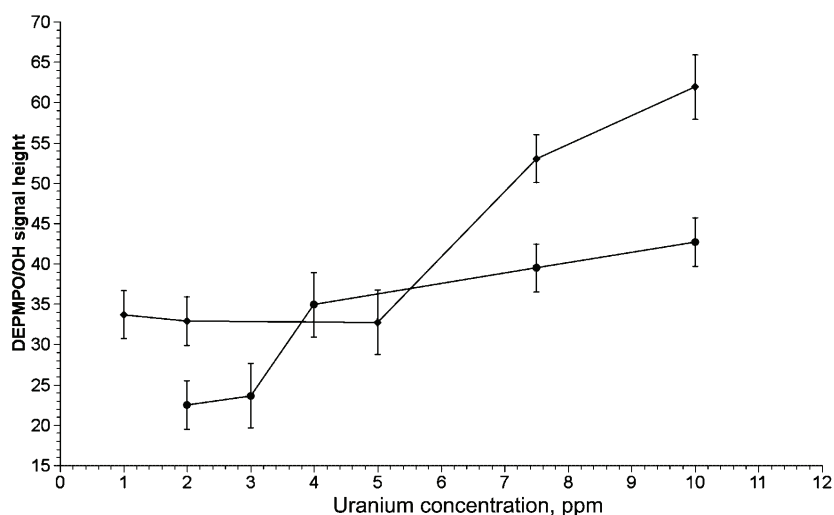


Fig. 6. Uranium concentration dependence of the signal of DEPMPO/OH, produced in solutions of uranyl acetate (●) and uranyl nitrate (◆), pH 10, by irradiation with UVB light.

The dependences between the signals of the DEPMPO/OH adducts and the concentration of uranium for solutions of uranyl acetate and uranyl nitrate in the presence of 0.010 M sodium carbonate, which is a realistic model for a natural aquatic environment, are shown in Fig. 7. The presence of 0.010 M carbonate maintains the pH value of the solution at pH 10.0, when carbonate complexes of uranyl are the only species present (Fig. 2). The found dependence of the DEPMPO/OH adduct signal on the uranium concentration could be a consequence of the replacement of hydroxyl ions in the coordination sphere of uranyl by carbonates. The dependencies for both compounds are linear, although with opposite slopes – negative for acetate and positive for nitrate.

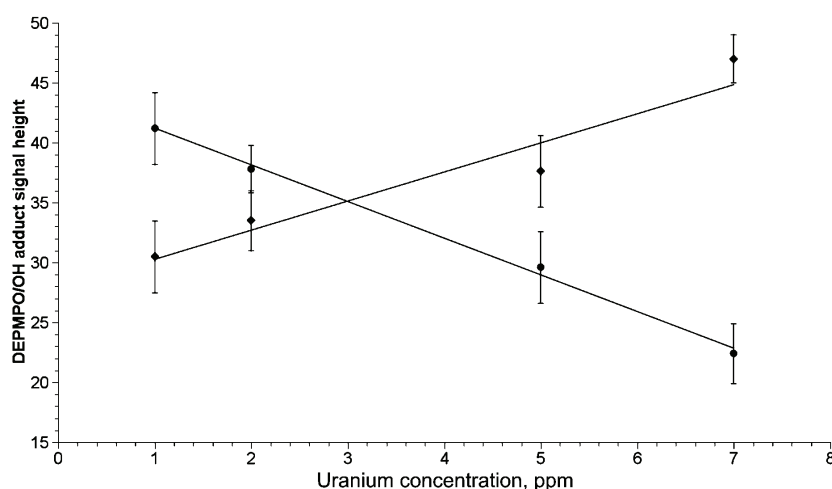


Fig. 7. Uranium concentration dependence of the signal of DEPMPO/OH, produced in solutions of uranyl acetate (●) and uranyl nitrate (◆) (0.010 M carbonate added) by irradiation with UVB light, on the uranium concentration.

The negative slope for uranyl acetate can be explained by a more efficient non-radiative energy transfer to acetate ions, probably *via* carbonates from the coordination sphere, which is favored by an increased concentration of acetates. Examples that this process is unfavorable from the aspect of the larger differences in energy with organic matter are numerous, including action on bioorganic polymers such as proteins and nucleic acids.²² The proposed mechanism is hydrogen abstraction from a reactive carbon atom, *i.e.*, a carbon atom in the states in the case of uranyl nitrate; hence there is a positive correlation between the amount of OH radicals and the concentration of uranium once the OH ions are removed from the coordination sphere.

Examples are uranyl ion interactions in the nearest vicinity of double bonds, hydroxyl, carbonyl or carboxyl group. Since it was shown in this study that •OH

are produced in uranyl solutions at physiological pH values, these mechanisms should be reconsidered to include the influence of hydroxyl radicals.

CONCLUSIONS

Using the EPR spin-trapping method, the production of OH radicals in uranyl solutions irradiated with ultraviolet light was unequivocally demonstrated. This is the first comprehensive study of this type, where their production was studied over a wide range of pH values (the only previous EPR study was constrained to a narrow, low pH range). Comparison of the obtained EPR results with those obtained by other authors using uranyl fluorescence quenching in aqueous solutions showed that production of OH radicals should be considered as one of the major mechanisms of UO_2^{2+} fluorescence decay. The effect of different counter ions and carbonate ions was also studied in order to assess their influence on production of hydroxyl radicals, attempting to reveal the mechanism of $^*\text{UO}_2^{2+}$ de-excitation. Although, further investigations are needed for a clarification of these mechanisms, the fact remains that potentially harmful OH radicals are produced under almost any circumstances encountered by biological systems, which should be taken into account when considering uranium toxicity.

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ИЗВОД

ПРОУЧАВАЊЕ ПРОИЗВОДЊЕ ОН РАДИКАЛА У ВОДЕНИМ РАСТВОРИМА УРАНИЈУМА ПОД ДЕЈСТВОМ УЛТРАЉУБИЧАСТЕ СВЕТЛОСТИ

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Циљ рада је испитивање услова при којим долази до продукције ОН радикала ($^*\text{OH}$) у воденим растворима уранијумових соли под дејством ултраљубичастог зрачења. Генерисање $^*\text{OH}$ је проучавано помоћу EPR спин трап методе у широком опсегу рН и при различитим концентрацијама уранијума у растворима уранил ацетата и уранил нитрата. Установљено је да је производња хидроксилних радикала повезана са дистрибуцијом уранијумских врста у раствору и да на сложен начин зависи од рН вредности раствора. Добијени резултати, упоређени са претходно публикованим подацима за гашење флуоресценције уранил јона, указују да хидроксилни радикали играју главну улогу у овом процесу. У циљу даљег разјашњавања механизма деексцитације побуђеног стања уранила, продукција $^*\text{OH}$ је испитивана и у присуству карбоната, односно под условима својственим животној средини. Продукција хидроксилних јона у растворима уранијума озраченим ултраљубичастим зрачењем одвија се преко различитих механизма. Чињеница да $^*\text{OH}$ настају у овим растворима мора се узети у обзир код разматрања токсичних ефеката уранијума.

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