Radiation Effects on the Property of ^{238}U(VI) or ^{239}Pu(IV) Doped Polyvinyl Alcohol Films Investigated by EPR and PAS

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Received: May 10, 2000; In Final Form: September 1, 2000

Electron paramagnetic resonance (EPR) and photoacoustic spectral (PAS) studies were conducted on pure polyvinyl alcohol (PVA) film, ^{238}U(VI) doped PVA film after gamma irradiation and ^{239}Pu(IV) doped PVA film after in-situ alpha irradiation. Studies on gamma irradiated U(VI) doped PVA film revealed the formation of U(V) complex and free radical $-CH_2-C^{\cdot}(OH)CH_2-$. The later was also formed in pure PVA film. The in-situ alpha-irradiation resulted in a broad line at g = 1.998 ± 0.001 in addition to weak lines due to $-C(^{\cdot}O)=CH_2-$ and $-CH_2-C^{\cdot}(OH)CH_2-$. The broad line appears to be due to high local concentration of these radicals which increased with longer in-situ irradiation. With long storage, a doublet, presumably due to interaction of $-C(^{\cdot}O)=CH_2-$ with I = 1/2 of ^{239}Pu got evolved.

1. Introduction

Polyvinyl alcohol (PVA) is reported to get grafted to vinyl monomers forming (graft) co-polymer when radical sites are introduced on PVA back bone. It was made possible due to an electron transfer reaction[1] using oxidant such as Ce^{4+}. The importance of such grafted co-polymers arises due to their hydrophilic characteristics. Furthermore, electron transfer reactions are known to play an important role in nonlinear optical properties in organic polymers. The electron transfer reaction involving photoexcited extrinsic metal ions is an important research area with wide range of interesting applications. It is well known[2] that U(VI) ion, UO_2^{2+}, is a strong photo oxidant reacting with alcohol to produce aldehyde/ ketone. It was reported[2-4] that in PVA solutions, reaction with the excited U(VI) ion, UO_2^{2+*}, normally occurs via abstraction of alpha hydrogen atom. This work suggests that UO_2^{2+} can be a good candidate to photo-initiate radical formation on PVA chain. So far this photoinduced reaction between U(VI) and PVA was reported only in aqueous solutions in which the excited state reaction was found to be highly pH dependent. In the present investigation we are interested in radiation chemical/ photo-physical properties of solid PVA films containing different metal ions. In view of above mentioned interesting reactions between UO_2^{2+} and PVA, we have initiated electron paramagnetic resonance (EPR) and photoacoustic spectral (PAS) studies of PVA film doped with actinide ions, U(VI) and ^{239}Pu(IV). These elements, analogous to Ce, exhibit multivalence and furthermore provide opportunity for continuous self irradiation particularly in the case of ^{239}Pu. The alpha and/ or external gamma irradiation producing both electronic excitation and ionisation should create conditions conducive for electron transfer reaction between these ions and PVA matrix. Such a study in solid state has not been reported.

EPR technique has been extensively used for identifying paramagnetic metal ions in different valence states, neutral radicals, radical cations/ anions formed when the organic system are subjected to ionising radiations and high energy photons like UV light. In aliphatic alcohols the hydrogen atom is removed by interaction of radiation yielding α-hydroxy alkyl and hydrogen atom. Polyvinyl alcohol on irradiation yields α-hydroxy alkyl radical which has been investigated previously.[5-7]

In this work we present evidence for the formation of U(V) on gamma irradiation and associated free radical formation. Results of the in-situ alpha-irradiation in the ^{239}Pu doped film will also be presented.

2. Experimetal

The solution of pure PVA was prepared by swelling it in quartz double distilled water. The solution was then warmed under infrared lamp at about 60˚C and stirred thoroughly until the polymer became completely soluble. $^{239}PuO_2$ was dissolved in HNO_3 under infrared lamp and later it was converted into water soluble chloride. The maximum amount of Pu is expected to be in Pu(IV) state in freshly prepared sample due to addition of a few drops of peroxide and was immediately added to PVA. Its disproportionation to a small extent yielding Pu(III) and Pu(VI) is not expected to be significant under these condition. The solutions were mixed together and stirred with a glass rod. Finally, the completely miscible solutions were poured on a level glass plate and dried in a glove box at room temperature for 48 hours to obtain homogeneous and bubble free ^{239}Pu(IV)-doped films.[8] A small portion of film was cut and sealed in the quartz glass tube. The outer surface of the quartz glass tube was decontaminated using teepol and dil. HNO_3. ^{238}U(VI)-doped PVA and pure PVA films were also made in a similar way as above. The isotopic composition of uranium is that of natural abundance and of Pu is 94.5% Pu-239 and 5.3% Pu-240. The EPR spectra were obtained at room temperature on an X-band spectrometer between 9-10 GHz. The films of UO_2^{2+} doped PVA and pure PVA were irradiated using a ^{60}Co source with dose rate 2 kGy/h. PAS spectra between 350-800 nm were recorded using home-built PA-spectrometer.[9]

3. Results

3.1. EPR Investigations. (i) Pure PVA film: The nonirradiated film did not show any EPR signal and also no absorption in PAS. On gamma-irradiation (dose 4 kGy), EPR spectrum showed presence of a triplet signal as shown in Figure 1. The spectrum was symmetrical with hyperfine coupling of 35 ± 2 G. The g value of the triplet is g = 2.003 ± 0.001. The intensity of the lines was in the ratio of 1:3:1.

(ii) U(VI)-doped PVA films: Virgin and stored films (over a period of one year) did not show any EPR signal. The self irradiation effects in this are not expected to be significant due

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to low specific radioactivity of ^{238}U. EPR spectra of gamma irradiated U(VI)-doped PVA film showed a broad and asymmetric line at g = 2.037 ± 0.001 and a weak triplet at g = 2.001 ± 0.001 ($a_H \approx 33 \pm 2$ G) as shown in Figure 2.

(iii) ^{239}Pu(IV) doped PVA film: Figure 3 shows the EPR spectra for ^{239}Pu(IV)-doped PVA, stored for different times. In freshly prepared sample, a sharp line g = 2.000 ± 0.001 along with an intense and broad line appeared at g = 1.998 ± 0.001, associated with satellite lines. In samples stored for nearly one year, these features got broadened and disappeared. However, a clear doublet with a separation of 120 G got developed. It was observed that ^{239}Pu(IV)-doped PVA film had become completely black and brittle on long storage for about three years.

3.2. Photoacoustic Spectral Investigations. Photoacoustic spectra have the potential to give electronic absorption spectral information on thin film and opaque samples. Photoacoustic spectrum (PAS) of nonirradiated U(VI)-doped PVA film showed intense optical absorption band at 420 nm and weak broad band at 620-650 nm. PAS spectrum of gamma irradiated U(VI)-doped PVA showed built-up in the intensity of broad band at 620-650 nm at the expense of 420 nm band. These spectra are shown in Figure 4.

4. Discussion

4.1. Radiation Effect in PVA. In aliphatic alcohols the hydrogen atom was reported to be removed by interaction of radiation yielding α-hydroxy alkyl radical and hydrogen atom. Polyvinyl alcohol on irradiation yields α-hydroxy alkyl radical which has been investigated.[5-7] The triplet EPR signal observed in gamma irradiated sample with intensity distribution of 1:3:1 is similar to that reported earlier.[5] Since it does not follow the intensity distribution of 1:2:1, it is clear that the signal is a composite one arising from at least two radicals of a 1:2:1 triplet and a singlet overlapping with central line. These results are similar to those reported by Ogawa[5] assigning the triplet to -CH$_2$-C$^\cdot$(OH)-CH$_2$-. For the signal with binomial intensity distribution 1:2:1 interaction of unpaired electron was attributed to two equivalent beta protons. The observation of triplet in this case instead of quintet was explained as due to streaic configuration with the original hydrogen bonds reverse almost completely so as to minimize the repulsion between unpaired spin and C-H bond. This makes one proton of each adjacent CH group predominantly interacts with unpaired spin density on p orbitals. The singlet at g = 2.003 ± 0.001 is assigned to oxygen center radical. Since singlet signal overlaps central part of triplet, this contributes to additional intensi-

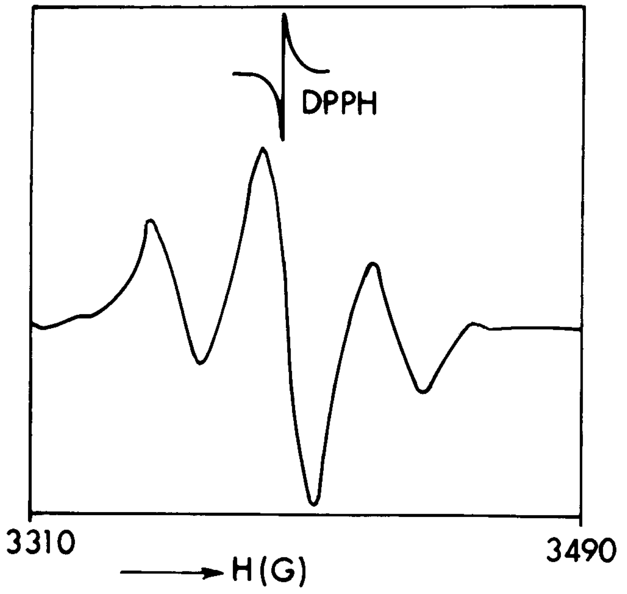


Figure 1. EPR spectrum of gamma irradiated (dose 4 kGy) PVA film at room temperature.

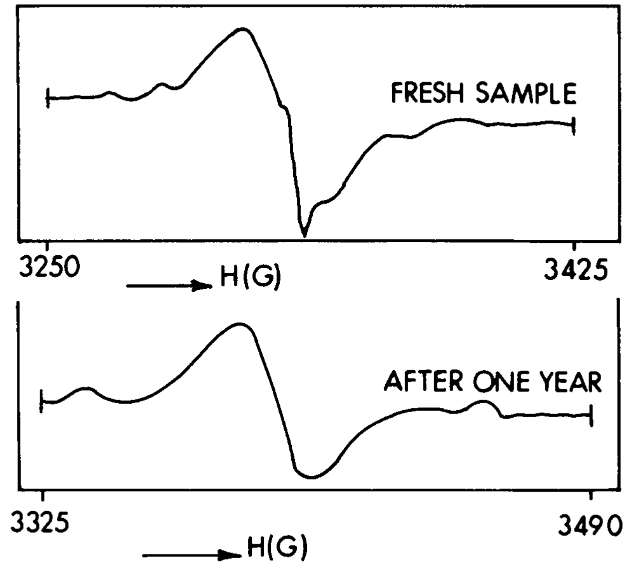


Figure 3. EPR spectra of ^{239}Pu(IV)-doped PVA film, stored for different times.

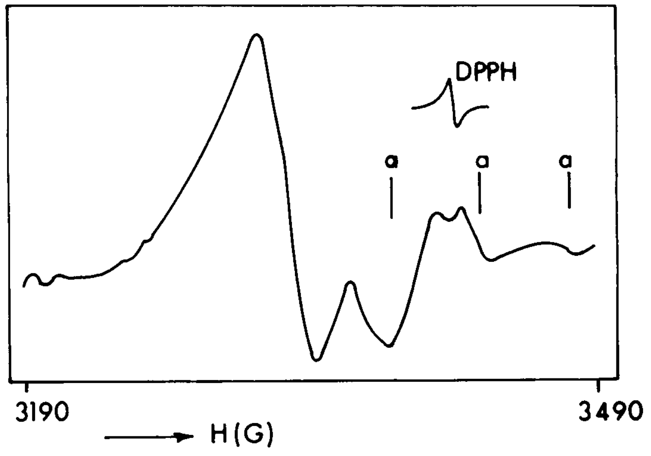


Figure 2. EPR spectrum of gamma irradiated (dose 4 kGy) U(VI)-doped PVA film. The weak triplet marked by 'a' at g = 2.001 ± 0.001.

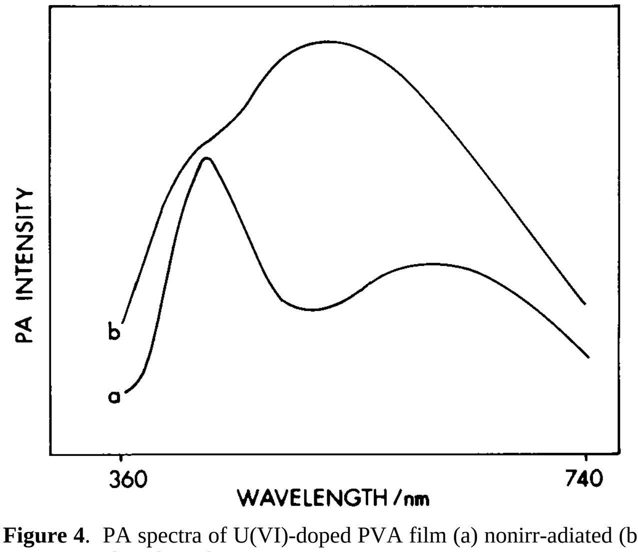


Figure 4. PA spectra of U(VI)-doped PVA film (a) nonirr-adiated (b) gamma irradiated at 4 kGy.

ty in the central region giving intensity distribution 1:3:1.

Pure PVA film irradiated at 77°K showed a broad unresolved quintet as expected due to $CH(OH)\text{-}C^{\cdot}H\text{-}CH(OH)$ a percursor for a alpha hydroxy alkyl radical[10] $\text{-}CH_2\text{-}C^{\cdot}(OH)\text{-}CH_2\text{-}$.

4.2. U(VI)-Doped PVA. The EPR spectrum of gamma irradiated U(VI)-doped PVA film showed the signal at $g = 2.037 \pm 0.001$, and weak triplet (marked by 'a' in Figure 2) with intensity distribution of 1:3:1 at $g = 2.001 \pm 0.001$ ($a_H \approx 33 \pm 2$G). It may also be noticed that g-value of this triplet is different from that discussed in 4.1. The paramagnetic species of uranium that can be generated by electron transfer is pentavalent uranium U(V). The pentavalent uranium, U(V), has one electron in 5f orbital and the crystal field interaction is given by the Hamiltonian.[11]

$$H_{\text{crystal field}} = H_{Oh} + \theta\,(O_2^{\,0} + \gamma O_2^{\,2}),$$

The parameters θ and γ represent axial and orthorhombic components in the crystal field, respectively, and O_2^0 and O_2^2 are the appropriate operator equivalents.[12]

Miyake[11] reviewed the magnetochemistry of U(V) complexes and compounds. U (V) was also reported to be stabilized at Nb sites in $LiNbO_3$ (Ref. 13) and at Ca site in CaO (Ref. 14) having octahedral coordination in both cases. An important aspect of U(V) in octahedral symmetry is its relatively long spin-lattice relaxation time facilitating the observation of its EPR at relatively higher temperature. Under octahedral symmetry, the lowest crystal field state of $5f^1$ is a doublet, Γ_2, which takes the form of Γ_7 under spin-orbit interaction. Miyake[11] discussed the effect of different extents of axial (C_{4v}) and orthorhombic (C_{2v}) distortions on the g value of U(V). In spite of low symmetry perturbations on octahedral crystalline field, the g value was reported to be nearly isotropic for small distortions. The absolute g value for overall octahedral symmetry is expected to be around 1.1 which remains constant up to a distortion (θ) of 800 cm^{-1} (for a fixed value of $\gamma = -0.2464$) beyond which the absolute value of g decreases.[13] In C_{4v} symmetry, the g value smoothly increases with increase in θ from the octahedral value of 1.1. Therefore g = 1.1 can be taken as a finger-print for near octahedral symmetry at the site of U(V). Deviation from this suggests a strong distortion. High value of θ and γ yield absolute value of g greater than 1.1. In the earlier report,[15] U(V) of $5f^1$ configuration in $LiNbO_3$ with uranium at Nb site having perfect octahedral coordination showed EPR signal at $g_{/\!/} = 0.70$, $g_{\perp} = 0.724$. The EPR signal of U(V) was reported[16] to be at $g_{\perp} = 2.5$ and $g_{/\!/} \approx 0.0$ on photo- and electrolytic-reduction of uranyl $(\text{dimethylformamide})_5(ClO_4)_2$ in dimethylformamide solution. Miyake et al[16] interpreted the results of U(V) in dimethylformamide on the basis of unpaired electron on U(V) complex with stronger bonding in equatorial plane. These authors very clearly rejected the possibility of formation of UO_2^+. These results suggest that there can be a large spread in the g-values expected for U(V) species. In the case of U(V) in $LiNbO_3$, the unpaired electron has more metal like character i.e. 5f character, giving large deviation in g from free electron value and is around -1.0. On the other hand in uranyl dimethylformamide perchlorate the U(V) in 5f has yielded a signal around g = 2.5. Therefore, it is clear that in U(V) complexes [Note-not uranyl complexes], the $|g_{\perp}|$ value can vary from 1.0 to 2.5 depending upon the strength of bonding in the equatorial plane. The g-value (absolute) obtained in the present study viz. 2.037 ± 0.001 suggests that uranium after electron transfer bridges the vinyl chains in such a way that it bonds in a direction perpendicular to O-U-O bond direction. This is taken as evidence for the role of uranium complex in crosslinking the polymer. It may be mentioned that it is the first EPR evidence for this phenomenon on trapping an electron.

In gamma irradiated U(VI)-doped PVA, in addition to U(V) signal, a weak triplet was also observed. In comparision with gamma irradiated pure PVA film, the intensity of triplet was less and also the g and A values are about 10% less. The reduction in g and A values suggests that it may be coupled to U(V) complex.

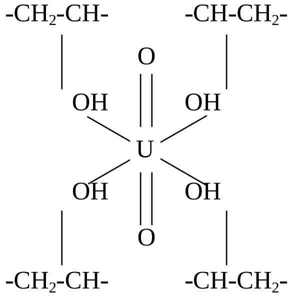
In view of these results following scheme is proposed for the radical formation in U(VI)-doped PVA film by gamma irradiation

$$[UO_2^{2+}]\text{:PVA--->}[UO_2^{2+}]^{*}\text{:PVA--->}(UO_2H)^{+} + \text{-}(CH_2\text{-}C^{\cdot}(OH)\text{-}CH_2)\text{-}$$

$$\downarrow$$

U(V) complex crosslinking
the polymer chain

The U(V) complex may have the following structure



The U(V) complex will be analogous to $[UO_6]^{7-}$ complex except for stronger bonding in the equatorial plane. The formation of U(V) was further confirmed by PAS experiment in which built up of 620-650 nm band was noticed due to conversion of U(VI) to U(V) on gamma irradiation.

4.3. ^{239}Pu(IV)-Doped PVA. The EPR spectrum of ^{239}Pu(IV)-doped PVA contained a rather broad feature due to the in-situ alpha irradiation, in addition to less intense other species containing hyperfine patterns. The predominant features of the EPR spectra are:(i) a broad line at $g = 1.998 \pm 0.001$, (ii) a sharp line at $g = 2.000 \pm 0.001$ along with satellites, and (iii) a doublet on long storage film with associated disappearance (or overlap with broad line) of sharp line. The second feature, however, gets buried in the broad spectrum over a long period of storage.

From a careful comparision of the spectra obtained in ^{239}Pu(IV)-doped PVA with that of gamma irradiated PVA, it is revealed that the line position of relatively sharper line along with satellites coincides with the triplet obtained at room temperature after gamma irradiation in pure PVA as discussed earlier: these radical ions are $\text{-}C^{\cdot}(=O)\text{-}CH_2\text{-}$ and $\text{-}CH(^{\cdot}O)\text{-}CH_2$. The latter radical contributes only to the intensity at the central line. The broad line, which keeps building on prolonged irradiation, is probably due to clustering of these radical ions in close proximity due to higher LET effect.

Over a prolonged alpha irradiation, it is quite probable that some of these centers with unpaired electron on oxygen get stabilized closer to the impurity ^{239}Pu(IV), interacting with the nuclear spin I=1/2 of ^{239}Pu(IV). This would result in the observation of a doublet. The hyperfine coupling constant value suggests significant covalency between ^{239}Pu(IV) and the radical ion $\text{-}CH(O^{\cdot})\text{-}CH_2\text{-}$. It is difficult, however, to unambiguously assign this to hyperfine interaction with ^{239}Pu. Electron nuclear double resonance studies would have showed this but could not be conducted due to low intensity of the signal.

5. Conclusions

The EPR investigations of gamma irradiated U(VI)-doped PVA film revealed the formation of U(V) complex and radical.

Concomitantly, radical of the type $-CH_2-C^{\cdot}(OH)-CH_2-$ is also formed in PVA.

Alpha irradiation effects in ^{239}Pu(IV)-doped PVA film produced different kind of radical compared to those by gamma irradiation. Furthermore, one of the radical centers probably got stabilized near ^{239}Pu(IV) (I = 1/2) resulting in doublet structure. The hyperfine coupling constant value suggests covalency between ^{239}Pu(IV) and the radical.

Acknowledgment. The authors are grateful to Dr. S. B. Manohar, Head, Radiochemistry Division, BARC, for encouragement during the course of this work.

References

(1) H. D. Burrows, S. J. Formosinho, and P. M. Saraiva, J. Photochem. Photobiol. A: Chem. **63**, 67 (1992).

(2) H. D. Burrows and T. J. Kemp, Chem. Soc. Rev. **3**, 139 (1974).

(3) D. Greatorex, R. J. Hill, T. J. Kemp, and T.J.Stone, J. Chem. Soc. Faraday Trans. 1 **68**, 2059 (1972).

(4) M. E. D. G. Azenha, H. D. Burrows, S. J. Formosinho, and M. G. M. Miguel, J. Chem. Soc. Faraday Trans. 1 **85**, 2625 (1989).

(5) S. Ogawa, J. Phys. Japan **16**, 1488 (1960).

(6) B. Sanjeeva Rao and M. R. Murthy, J. Polymer science part B: Polymer Physics **25**, 1897 (1987).

(7) R. J. Abraham and D. H. Whiffen, Trans. Faraday Soc. **54**, 1291 (1958).

(8) Mithlesh Kumar, A. R. Dhobale, Mukesh Kumar, and M. D. Sastry, J. Polymer science part B: Polymer Physics **35**, 187 (1997).

(9) A. R. Dhobale, T. P. Chaturvedy, S. Venkiteswaran, and M. D. Sastry, Solid State Physics (India) **38C**, 455 (1995).

(10) H. Hase and H. Yamaoka, Rad. Effects **19**, 195 (1973).

(11) C. Miyake, in *Handbook on the Physics and Chemistry of Actinides* edited by A. J. Freeman and C. Keller (Elsevier Science Publishers, Amsterdam, 1991), Ch.7, p.337.

(12) A. F. Leung and Y. Poon, Can. J. Phys. **55**, 937 (1977).

(13) W. Burton Lewis, H. G. Hecht, and M. P. Eastman, Inorg. Chem. **12**, 1634 (1973).

(14) V. Natarajan, T. K. Seshagiri, and M. D. Sastry, Pramana-Journal of Physics **47**, 325 (1996).

(15) N. K. Porwal, Mithlesh Kumar, and M. D. Sastry, Pramana-Journal of Physics **47**, 481 (1996).

(16) C. Miyake, Y. Yamana, S. Imoto, and H. O. Nishiguchi, Inorganica Chimica Acta **95**, 17 (1984).