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Some Parametric Studies on Separation of Palladium from Perchloric Acid Medium by Radiolytic Reduction

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Some Parametric Studies on Separation of Palladium from Perchloric Acid Medium by Radiolytic Reduction

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Abstract: The radiolytic reduction of palladium ions to palladium metal in perchloric acid solutions has been studied with the aim of separating palladium from aqueous acidic waste. Fraction of Pd separated out as precipitate has been studied as a function of initial Pd concentration and strength of $HClO_4$. Addition of t-butanol to the system has been found to cause substantial enhancement in the amount of Pd precipitated as compared to that in its absence. At a given absorbed dose, the extent of Pd separated is found to increase with the concentration of $HClO_4$ in presence of t-butanol. However, the converse is true for the radiolysis in absence of t-butanol. The decrease in the extent of reduction of Pd(II) to Pd(0) has been found to be due to increasing formation of chloride ions that tend to form reduction resistant cholorocomplexes of Pd. This is supported by the red-shifting in the absorption bands of $Pd(ClO_4)_2$ observed for the spectra of gamma radiolysed solutions of Pd(II) at higher $HClO_4$ concentrations. External addition of chloride ions to aqueous

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Pd(II)/$HClO_4$ system even in presence of t-butanol has been found to cause substantial inhibition to the radiolytic reduction of Pd(II) owing to formation of reduction-resistant complexes. Correspondingly, the addition of nitrate ions to Pd(II)/$HClO_4$/t-butanol system showed inhibition effect at much greater stoichiometric amount of nitrate.

Keywords: Palladium, γ-radiolysis, radiation chemical yield (G value), chloride ions, nitrate ions, perchloric acid

INTRODUCTION

Radiation-chemical behavior of Pd is of importance while considering the recovery of Platinum group metals (PGM) from high level wastes (HLW) arising from reprocessing of spent nuclear fuel. Significantly greater abundance of Pd in nuclear waste solutions as compared to other natural resources has shown a need to develop a suitable recovery method for this noble metal. The radiolytic processes occurring in the aqueous and organic systems involving PGM have received very little attention. Gamma radiolysis of aqueous solutions is known to generate various redox species through the radiolysis of water. Under suitable solution conditions the system could be made almost exclusively reducing or oxidizing depending on the solution composition and pH. The net reducing condition generated by use of appropriate scavengers for oxidizing radicals in the radiolysis of aqueous system will facilitate precipitation of noble metals. Thus, the system is amenable to separation of some noble metals under suitable gamma radiolytic conditions. Over the past decades or so, these studies have been primarily focussed on the preparation of noble metal clusters and colloids (1–7). However, less attention has been focused on achieving separation of metals in the form of precipitate.

The presence of intense radiation and highly acidic environment of Pd in the radioactive waste solutions makes the study of its radiation chemistry a challenging research problem. Some studies on the radiation-chemical behaviour of Pd in $HClO_4$ without any additive have been carried out by Vladimirova et al (8). The studies aimed at understanding the occurrence of radiolytic transformations in acidic solutions of the noble metals with commonly accompanying impurities would also be of great help in the retrieval of these metal ions before vitrification of the high level radioactive waste. Vladimirova et al have observed that in contrast to $HClO_4$ medium, the radiolytic reduction of Pd(II) to metal form is not feasible in HNO_3 medium (9). It is important to investigate the qualitative as well as quantitative effect of the presence of NO_3^- and Cl^- ions on the radiolytic reduction of Pd(II) present in a relatively uncomplexing medium like $HClO_4$. It will be helpful in predicting the radiation-chemical behaviour of these metal ions in a typical waste from reprocessing operations. The study reported in the paper deals with parametric effects pertaining to the radiolytic reduction of Pd (II) in aqueous $HClO_4$ solutions containing t-butanol. The data obtained on the variation of radiolytic Pd(II) consumption yield

$G_{[\text{-Pd(II)}]}$ as a function of added chloride ion and nitrate ion concentrations, are also presented and discussed here.

EXPERIMENTAL

Reagents and Chemicals

Palladium perchlorate was prepared by dissolving $PdCl_2$ in HCl and fuming it several times with $HClO_4$, until a solution with typical absorption maximum at 379 nm, was obtained (10). All other chemicals used were of guaranteed reagent grade.

Gamma Irradiation

A ^{60}Co gamma source with a dose rate of 4.2 kGy/h has been used for the irradiation. The measurement of the absorbed dose was carried out using Fricke dosimetry, employing freshly prepared air saturated solution containing 1.0×10^{-3} M ferrous ammonium sulfate, 0.47 mol dm^{-3} H_2SO_4 and 1.0×10^{-3} M sodium chloride. To determine the absorbed dose the dosimeter solution in a glass container (i.d. $\approx$ 8 mm) is placed in radiation field for a measured length of time, and the yield of Fe^{3+} ions is measured spectrophotometrically at 304 nm. Using extinction coefficient of 2204 M^{-1} cm^{-1} (25°C) for Fe^{3+} ions, and $G(Fe^{3+}) = 15.5$, the final dose equation can be expressed as

$$D_D = 2.77 \times 10^2 \times \Delta A/1 \qquad (1)$$

Where, D_D is the dose in Gy, ΔA is increase in absorbance at 304 nm and l is the optical path length in cm (11).

Radiolysis in aqueous medium results in both oxidizing and reducing transient species. Dissolved oxygen in aqueous solutions ($\sim 2 \times 10^{-4}$ M) scavenges some of the reducing species, thus affecting the Pd(II) to Pd(0) reduction process. N_2 gas was bubbled in the solutions (for ~20 minutes) before γ-irradiation in closed vials, to minimize this effect. Gamma-radiolytic reduction studies in the presence of 0.26 M t-butanol to scavenge strongly oxidizing hydroxyl radicals, were also carried out.

Preparation of Working Solutions

A stock solution of 2.2×10^{-2} M $Pd(ClO_4)_2$ in 4 M $HClO_4$ was used for making working solutions of 1.0×10^{-3} M $Pd(ClO_4)_2$ in 0.5 M $HClO_4$, normally employed for various parametric studies. This was prepared by the addition of required amount of $HClO_4$ and dilution with nano-pure water. The effect of change in concentrations of $Pd(ClO_4)_2$ (at a constant $HClO_4$

concentration of 0.5 M) and $HClO_4$ (at a fixed $Pd(ClO_4)_2$ concentration of 1.0×10^{-3} M), on the reduction of Pd(II) was also studied.

Effect of Chloride and Nitrate Ions Addition

The effect of chloride ion (1.0 to 5.0×10^{-3} M) and nitrate ion (2.0×10^{-3} to 5.0×10^{-2} M) concentrations on the radiolytic reduction of Pd(II) in the solution containing 1.0×10^{-3} M $Pd(ClO_4)_2$, 0.5 M $HClO_4$ and 0.26 M t-butanol have also been investigated.

Spectrophotometric and Pd Concentration Measurements

All these measurements were made after filtration of the gamma irradiated solutions through a milipore filter in the presence of air. Suitable aliquots of the studied solutions were isolated and kept in dark to serve as respective controls. The visible spectra of the control and radiolysed solutions were recorded using Shimadzu model UV-240 spectrophotometer within 2 hours after the filtration. The residual concentration of Pd(II) in the irradiated solution after the filtration was analysed by Atomic absorption spectroscopy (AAS) using Varian Techtron model AA-4 updated to AA-6 model instrument having a 100 mm (air + acetylene) burner head with manual gas controls. Flow of air/acetylene was 6/2.25 L/min., while lamp current was maintained at 5 mA. Absorbance of dissolved Pd was measured at wavelength of 242.8 nm with a bandwidth of 0.2 nm. The observation height is kept at 5 mm. The standard calibration runs for Pd in the concentration range of 2–8 μg/mL prepared from pure Pd metal powder were performed. Based on this calibration the actual concentration of Pd in test solutions were estimated with an accuracy of $\pm 2\%$. All the above measurements were repeated three times at different time points.

RESULTS AND DISCUSSION

Palladium being a noble metal, Pd(II) ions have natural tendency to go to Pd(0) state, which may be induced by thermal and/or photochemical means. Under the ambient conditions, the aqueous $Pd(ClO_4)_2/HClO_4$ solution was quite stable and did not show practically any change in its absorption spectrum on aging for a few days. Whereas, the solutions in the presence of t-butanol showed a slow blue shift in the absorption maximum along with precipitation of black metallic particles of Pd(0) on aging. Thus, only fresh solutions were used in all these experiments (specially in the presence of t-butanol) to minimize errors due to the slow thermal and/or photochemical reduction of Pd(II) under ambient conditions (i.e. non-radiolytic reduction).

Figure 1 shows the typical UV-Visible absorption spectra of control and gamma irradiated (240 kGy) aqueous 1.25×10^{-2} M $Pd(ClO_4)_2$ solution containing 0.5 M $HClO_4$ (N_2 saturated) both in the absence and presence of 0.26 M t-butanol. Radiolysis of solution of $Pd(ClO_4)_2$ in the absence of t-butanol showed about 30% reduction in the 379 nm absorption band intensity along with the formation of black precipitate (Fig. 1B), indicating partial removal of dissolved Pd(II). Whereas, radiolysis in the presence of t-butanol, resulted in complete precipitation of dissolved Pd in the form of black particles. This is reflected by the negligible absorbance at 379 nm of the corresponding solution after radiolysis (Fig. 1D). The radiation-chemical yield ($G_{[\text{-Pd(II)}]}$) was estimated using identical solutions of $Pd(ClO_4)_2$ after gamma irradiation for optimum doses. It was observed that $G_{[\text{-Pd(II)}]}$ was only 0.17 in the absence of t-butanol while that in its presence had a value of 1.5. This implies that the addition of t-butanol leads to substantial increase in the extent of removal of dissolved Pd(II) by the radiolytic effect in contrast to that in its absence.

Effect of $HClO_4$ Concentration

The UV-Visible absorption spectra of γ-irradiated aqueous 1.0×10^{-3} M $Pd(ClO_4)_2$ solution at increasing $HClO_4$ concentrations (from 0.5 to 4.0 M) are shown in Fig. 2. These spectra have been recorded after filtering the precipitated Pd(0) from the irradiated solutions (dose = 123 kGy). The spectrophotometric observations of the experiment are presented in Table 1. The absorption spectra show the formation of two absorption bands upon radiolysis, one in the UV region, and the other in the Visible region (404–412 nm) The λ_{max} of both the absorption bands was found to shift towards

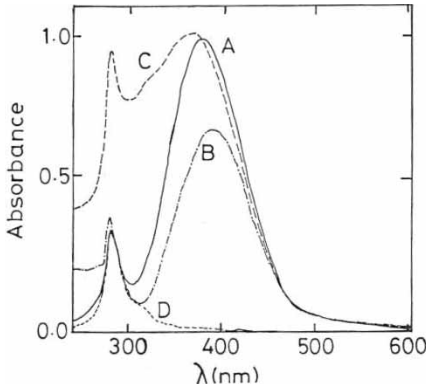

Figure 1. UV-Visible absorption spectra of N_2-bubbled aqueous solution containing 1.25×10^{-2} M $Pd(ClO_4)_2$ and 0.5 M $HClO_4$ (A) Unirradiated, (B) Irradiated (240 kGy); In the presence of 0.26 M t-butanol (C) Unirradiated and (D) Irradiated (240 kGy).

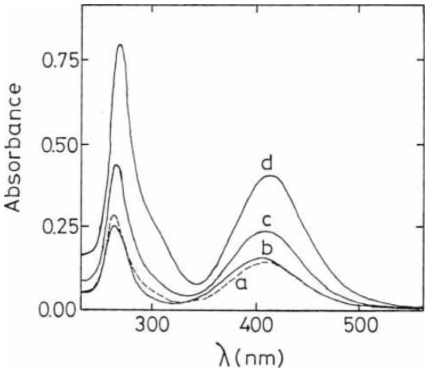

Figure 2. γ-Radiation induced changes in the UV-Visible absorption spectra of N_2-bubbled aqueous 1.0×10^{-3} M $Pd(ClO_4)_2$ solution as a function of $[HClO_4]$ (a) 0.5, (b) 1.0, (c) 2.0 and (d) 4.0 M (Dose = 123 kGy).

red region with increase in $HClO_4$ concentration. It shows the maximum shift in the λ_{max} of the visible absorption band from 404 to 412 nm as $[HClO_4]$ increases from 0.5 to 4.0 M. Whereas, the unirradiated $Pd(ClO_4)_2$ solution have the characteristic absorption band with λ_{max} at 379 nm. The observed increase in the intensity of the visible absorption band with $[HClO_4]$ indicates decrease in the yield of Pd(0). It was also confirmed from the amount of Pd(0) precipitated on radiolysis, which was found to be inversely proportional to the initial $[HClO_4]$ in the solution. Similarly, it has also been observed that for a fixed amount of initial $[HClO_4]$, the extent of the red shift in the gamma radiolysed solution is proportional to the absorbed dose (data not presented here). The probable cause of the red shift in the absorption maximum could be the chloride ions formed from the radiolysis of $HClO_4$, which are known to form a number of chloro-complexes with Pd(II) depending upon the $[Pd(II)]/[Cl^-]$ ratio (10). In order to confirm it, spectrophotometric measurements were made with a solution of $Pd(ClO_4)_2/$

Table 1. Effect of $HClO_4$ concentration on the absorption characteristics of aqueous $Pd(ClO_4)_2$ solution, induced by gamma irradiation

	Absorbance (λ_{max}) after gamma radiolysis	
Initial $[HClO_4]$ (M)	(in UV region)	(in Visible region)
0.5	0.25 (265.4 nm)	0.15 (404 nm)
2.0	0.45 (267.4 nm)	0.235 (408 nm)
4.0	0.79 (269.8 nm)	0.407 (412 nm)

Dose = 123 kGy.
$[Pd(ClO_4)_2] = 1.0 \times 10^{-3}$ M.

$HClO_4$ spiked with increasing concentrations of chloride ions (as NaCl). Here also, the red shifts in the absorption spectra of the solutions, analogous to that in Fig. 2, were observed. The extent of red-shift was found to be in proportion to the amount of chloride ions added to the starting solution with absorption maximum at 379 nm.

Since the extent of red-shift observed in the spectra of $Pd(ClO_4)_2$ due to radiolysis is proportional to the initial [$HClO_4$] and absorbed dose, it becomes increasingly clear that the radiolytic changes in $Pd(ClO_4)_2/HClO_4$ system are attributable to radiolytic generation of chloride ions from $HClO_4$. It appears that the changes in the visible spectrum are caused by the complexation of the chloride ions with remaining Pd(II) in the solution.

An interesting aspect of the study was the observation that the radiolytic removal of Pd(II) in the presence of t-butanol was also found to be dependent on the concentration of $HClO_4$, but the effect was opposite to that observed in the absence of t-butanol. The results are summarized in the Table 2. It may be noted that the amount of Pd(II) left in the solution after radiolysis, decreased with increase of $HClO_4$ concentration in the starting solution. The observed results in the presence of t-butanol are due to the combined effect of both the radiolytic reduction and the thermal and/or photochemical reduction under ambient conditions (i.e. the non-radiolytic reduction). Examination of the UV-Visible absorption spectra of the control and radiolyzed samples of $Pd(ClO_4)_2$ solutions with increasing $HClO_4$ concentrations has indicated that in the presence of t-butanol, the kinetics of the non-radiolytic reduction is also dependent on the concentration of $HClO_4$. In the presence of t-butanol, the contribution of the non-radiolytic reduction component enhances significantly with increase in $HClO_4$ concentration.

Effect of $Pd(ClO_4)_2$ Concentration

Table 3 shows the variation of $G_{[Pd(0)]}$ with initial concentration of $Pd(ClO_4)_2$ in solutions containing 0.26 M of t-butanol. The G value for the formation of

Table 2. Effect of increasing [$HClO_4$] on removal of dissolved Pd(II) in the presence of t-butanol

[$HClO_4$] (M)	Residual Pd(II) in solution after irradiation (ppm)
0.5	—
1.7	61
3.4	23
4.0	17

Initial [$Pd(ClO_4)_2$] = 1.0×10^{-3} M, i.e. = 110 ppm.
[t-butanol] = 0.26 M.
Dose = 5.20 kGy.

Table 3. Variation of $G_{[Pd(0)]}$ with initial $[Pd(ClO_4)_2]$ in the presence of t-butanol

$[Pd(ClO_4)_2]$ (M)	$G_{[Pd(0)]}$	Dose (kGy)
1×10^{-4}	0.2	10
1.0×10^{-3}	0.4	50
1.25×10^{-2}	1.5	200

[t-butanol] = 0.26 M.
$[HClO_4] = 0.5$ M.

Pd(0) in the solutions were higher at higher initial concentrations of Pd(II), which is as expected. At higher initial Pd(II) concentrations, the radiolytically produced reducing species are more efficiently utilized in the reduction process of Pd(II) to Pd(0), rather than getting consumed in other competing reactions which do not lead to Pd(0) formation.

Post Irradiation Formation of Pd(0)

A second interesting fact noted was the acceleration in the rate of precipitation of Pd(0) from the solutions in the post irradiation intervals, in the presence of t-butanol (Table 4). The greater the initial gamma dose, the higher was the yield of separated Pd(0) in the form of black particles, in the post irradiation period. However, over the entire period of observation, i.e. up to 74 hours, the non-radiolytic reduction [with respect to Pd(0) formation] in the unirradiated solution was found to be much lower, under the studied experimental conditions.

Some organic species resulting from radiolysis of t-butanol may be responsible for the post irradiation enhancement of Pd(II) separation.

Table 4. Dependence of post irradiation reduction on the initial gamma radiolysis time

Time of irradiation (min)	Residual Pd(II) concentration (in ppm) left in the solution after post irradiation time of:		
	0 hour	2 hour	74 hour
0 (control)	11.1	11.1	10.7
4	11.1	10.9	8.7
12	8.7	8.3	2.3
18	7.2	6.6	1.6

$[Pd(ClO_4)_2] = 1.08 \times 10^{-4}$ M (i.e. 11.1 ppm).
[t-butanol] = 0.26 M.
Dose Rate = 4.2 kGy/h.

In order to examine the effect of Pd(II) on the radiolytic transformation of t-butanol, a solution containing $HClO_4$ and t-butanol in presence and absence of $Pd(ClO_4)_2$ was radiolysed for a dose where Pd(0) precipitation was near completion i.e. about 90%, as checked by AAS analysis and the absorption spectra are shown in Fig. 3. It appears as if Pd(II) ions catalyze/enhance the radiation-chemical yield of unknown species absorbing in UV region below ~340 nm with λ_{max} at 267 nm and a small hump at ~310 nm. This build-up of absorbance in the UV region could be attributed:

i. either to unusual valence state of Pd, which is stable to oxidation by air or
ii. to organometallic species that result from reaction of a complexing species generated from t-butanol with Pd(II) in the presence of $HClO_4$.

It should be noted that the Pd(II) has strong tendency to form sigma bonds with carbon and is also known to readily form pi-allyl species (12).

Probable Mechanism

To understand the phenomenon of radiolytic reduction in aqueous $Pd(ClO_4)_2/HClO_4$ system, one should first consider the primary effect of γ-radiation on different constituents of the system. The major components of this system are: water (~55 M), $HClO_4$ (0.5–4.0 M) and a very low molar concentration (~10^{-3} M) of Pd(II). Hence, it is the net reactivities of the radiolytic products of water (to a major extent) and perchloric acid (to a

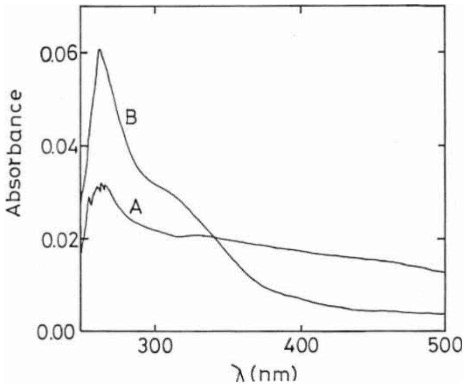

Figure 3. UV-Visible absorption spectra of γ-irradiated (16.8 kGy) N_2-bubbled aqueous solution of 0.5 M $HClO_4$ containing 0.26 M t-butanol (A) In the absence of Pd (II), and (B) filtered solution with 7 ppm residual Pd(II) obtained by starting with 60 ppm Pd(II).

much smaller extent), which will determine the ultimate extent of redox changes in the system.

$$H_2O \rightsquigarrow H^{\bullet}, OH^{\bullet}, e^-_{aq} \quad (2)$$

$$HClO_4 \rightsquigarrow ClO_4^{\bullet}, ClO_3^{\bullet}, O^{\bullet}, O_2^-, H^{\bullet}, OH^{\bullet}, e^-_{aq} \quad (3)$$

$$ClO_4^{\bullet} \longrightarrow O_2 + ClO_2^{\bullet} \quad (4)$$

$$ClO_2^{\bullet} \longrightarrow Cl^{\bullet} + O_2 \quad (5)$$

$$OH^{\bullet} + OH^{\bullet} \longrightarrow H_2O_2 \quad (6)$$

$$Cl^{\bullet} + H_2O_2 \longrightarrow Cl^- + H^+ + HO_2^{\bullet} \quad (7)$$

$$Cl^{\bullet} + Cl^- \longrightarrow Cl_2^{\bullet -} \quad (8)$$

Among the transient species formed by radiolysis of $HClO_4$, $ClO_4^{\bullet}$, $ClO_3^{\bullet}$, $ClO_2^{\bullet}$, $O^{\bullet}$, O_2^-, $OH^{\bullet}$, $Cl_2^{\bullet -}$, etc., are all oxidizing in nature, whereas, $H^{\bullet}$ and e^-_{aq} are of reducing nature. However, radiolysis of water gives reducing $H^{\bullet}$ and e^-_{aq} radicals along with oxidizing $OH^{\bullet}$ radicals. It is observed that the radiolytic formation of Pd(0) precipitate do takes place in the absence of quenchers of strongly oxidizing $OH^{\bullet}$ radical, like t-butanol, but its kinetics is quite slow. Thus, the combined effect of all these reducing and oxidizing radicals produced in the system, results in an overall reducing environment.

The formation of chloride ions may result from the sequence of reactions (3) to (7) as given above. The reduction of Pd(II) may be described by following reactions:

$$Pd(II) + H^{\bullet}/e^-_{aq} \longrightarrow Pd(I) + H^+/H_2O \quad (9)$$

In the presence of $HClO_4$, most of the e^-_{aq} is converted to $H^{\bullet}$ atom by the reaction (10).

$$e^-_{aq} + H^+ \longrightarrow H^{\bullet} \quad (10)$$

Thus, $H^{\bullet}$ atom is the main reducing agent under the studied experimental conditions. The Pd(I) species can ultimately lead to the separation of Pd(0) metal as fine black precipitate, via dismutation of Pd(I) followed by aggregation of Pd(0) species.

$$2Pd(I) \longrightarrow Pd(II) + Pd(0) \quad (11)$$

$$nPd(0) \longrightarrow Pd_n(0) \quad (12)$$

In the absence of $OH^{\bullet}$ radical scavenger, oxidation of Pd(I) and Pd(II) can decrease the yield of Pd(0) formation by reactions (13) and (14). Other oxidizing radicals present in the system may also initiate these reactions.

$$\mathrm{Pd(I)} + \mathrm{OH}^{\bullet} \longrightarrow \mathrm{Pd(II)} + \mathrm{OH}^{-} \tag{13}$$

$$\mathrm{Pd(II)} + \mathrm{OH}^{\bullet} \longrightarrow \mathrm{Pd(III)} + \mathrm{OH}^{-} \tag{14}$$

This is the reason for the observed lower $G_{[\text{-Pd(II)}]}$ value of 0.17, under the experimental conditions of Fig. 1B.

However, in the presence of t-butanol, the yield of $\mathrm{Pd_n(0)}$ is enhanced significantly, as it converts strongly oxidizing $\mathrm{OH}^{\bullet}$ radicals into relatively less reactive alcohol radicals, thus suppressing reactions (13) and (14).

$$\mathrm{CH_3C(CH_3)_2OH} + \mathrm{OH}^{\bullet} \longrightarrow {}^{\bullet}\mathrm{CH_2C(CH_3)_2OH} + \mathrm{H_2O} \tag{15}$$

Electron paramagnetic resonance (EPR) investigations have shown that the presence of similar alcohols can also result in scavenging of various oxidizing species obtained from radiolysis of $\mathrm{HClO_4}$ (13).

EFFECT OF CHLORIDE AND NITRATE IONS

In contrast to nitrate ions, the addition of chloride ions to 1.0×10^{-3} M $\mathrm{Pd(ClO_4)_2}$ solution containing 0.5 M $\mathrm{HClO_4}$ results in gradual shift in the absorption maximum from 379 nm to longer wavelengths viz. 421 nm at $[\mathrm{Cl^-}] = 5 \times 10^{-3}$ M, with corresponding changes in extinction coefficients. In general, the complexes of Pd(II) with $\mathrm{Cl^-}$ are very strong compared to those with nitrate ions. Figure 4 shows the absorption spectra of gamma irradiated aqueous 1.0×10^{-3} M $\mathrm{Pd(ClO_4)_2}$, 0.5 M $\mathrm{HClO_4}$ and 0.26 M t-butanol

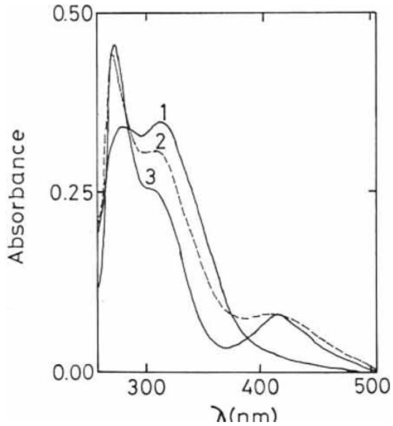

Figure 4. Effect of $\mathrm{Cl^-}$ concentration on the γ-radiolysis of $\mathrm{N_2}$-bubbled aqueous 1.0×10^{-3} M $\mathrm{Pd(ClO_4)_2}$, 0.5 M $\mathrm{HClO_4}$, 0.26 M t-butanol solution at [NaCl] (1) 0, (2) $1. \times 10^{-3}$, and (3) 5.0×10^{-3} M (Dose = 5.2 kGy).

solution in presence of varying concentrations of Cl^- ions. It is clearly seen that with increasing stoichiometric concentration of chloride ion the radiolytic reduction of Pd(II) is decreased.

Figure 5 shows the effect of t-butanol and nitrate ions on the UV-Visible absorption spectra of aqueous 1.0×10^{-3} M $Pd(ClO_4)_2$, containing 0.5 M $HClO_4$. The typical absorption spectra obtained on gamma irradiating these solutions for 5.2 kGy, are also shown in the figure. Addition of 0.26 M t-butanol to aqueous $Pd(ClO_4)_2/HClO_4$ solution [curve (a) with usual 379 nm Pd(II) absorption band] results in solution with spectrum (b) having absorption in UV region. Further addition of 5.0×10^{-3} M $NaNO_3$ gives solution with similar spectral features, except higher absorbance in the UV region due to the characteristic absorption of nitrate ions [curve (c)]. γ-Radiolyzed solutions in the absence and presence of nitrate ions [curve (d) and (e) respectively], also have similar features with absorption maxima at around 312 nm. This implies that small amount of added nitrate ions has relatively no ligand effect on the Pd(II) in $HClO_4$ medium.

The formation of the chlorocomplexes could result in reduced reactivity of the Pd(II) towards the H atom, which is a primary reducing species radiolytically generated under the present experimental conditions. The formation

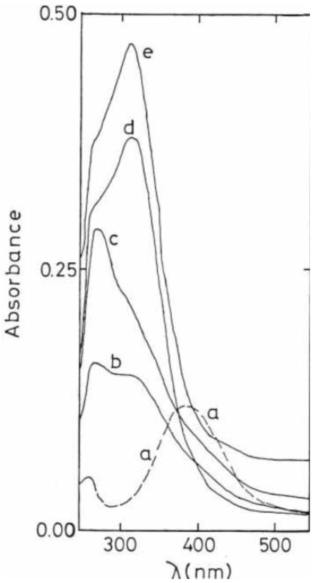

Figure 5. UV-Visible absorption spectra of unirradiated N_2-bubbled aqueous 1.0×10^{-3} M $Pd(ClO_4)_2$ solution containing 0.5 M $HClO_4$—(a), in the presence of 0.26 M t-butanol—(b), and in the presence of 0.26 M t-butanol along with 5.0×10^{-3} M $NaNO_3$—(c). While curve—(d) and—(e) show the spectra of γ-irradiated solutions (b) and (c) respectively (Dose 5.2 kGy).

Table 5. Effect of addition of Cl^- and NO_3^- ions on $G_{[\text{-Pd(II)}]}$

Concentration of chloride or nitrate ions (10^{-3} M)	$G_{[\text{-Pd(II)}]}$	
	Chloride effect	Nitrate effect
0.0	0.40	0.40
2.0	0.30	0.30
5.0	0.10	0.30
10.0	—	0.30
20.0	—	0.30
50.0	—	0.10

$[Pd(ClO_4)_2] = 1.0 \times 10^{-3}$ M, $[HClO_4] = 0.5$ M.
[t-butanol] = 0.26 M.

constants of the Pd(II) complexes with nitrate ions are much lower. Therefore, any parallel inhibiting effect by the NO_3^- would require higher concentration of the nitrate as compared to the chloride ion. The observed greater reducibility of Pd(II) ions even in presence of NO_3^- ions in manifold higher stoichiometric concentrations, proves its relatively poorer complexing strength (ligand strength) towards Pd(II) ions. Inhibition due to nitrate ions is possibly due to the fraction of oxidizing transients generated by its radiolysis that tend to nullify the reducing effect generated by the radiolysis of remaining matrix components (water being major).

Table 5 shows the effect of Cl^- and NO_3^- ions on the radiolytic removal of Pd(II) from the solutions i.e. $G_{[\text{-Pd(II)}]}$. It may be noted that with increase in the concentration of Cl^- ion the $G_{[\text{-Pd(II)}]}$ uniformly decreases. However, at a given concentration of chloride or nitrate ions, the inhibitive effect on the radiolytic removal of Pd(II) was found to be stronger in case of chloride ions. At around $[Cl^-]/[Pd(II)] = 5$, $G_{[\text{-Pd(II)}]}$ is about $1/4$ of the value obtained when $[Cl^-] = 0$. The reduction in $G_{[\text{-Pd(II)}]}$ due to 5 mM of chloride ion is roughly equal to that observed with the addition of 50 mM of nitrate ion under identical experimental conditions. The greater tendency of chloride to inhibit the radiolytic reduction of Pd(II) parallels the change in the redox potential of Pd^{2+} accompanying complexation with the added Cl^- ion.

$$Pd^{2+} + 2e^- = Pd \quad E^0 = +0.987\ V \tag{16}$$

$$[PdCl_4]^{2-} + 2e^- = Pd + 4Cl^- \quad E^0 = +0.620\ V \tag{17}$$

CONCLUSIONS

It has been demonstrated that separation of Pd(II) from $HClO_4$ solution is feasible by the gamma radiolytic reduction method. The rate of Pd(II) separation decreases with increasing absorbed dose. Also at a given absorbed dose, the radiolytic separation yield of Pd(0) diminishes sharply with increasing $HClO_4$ strength (from 0.5 M to 4 M). Both these observations are attributed to the formation of reduction resistant chloro-complexes of Pd(II) produced by the chloride ions originating from the radiolysis of $HClO_4$. This has been validated by carrying out radiolysis experiments at varying ratio of $Pd(ClO_4)_2/Cl^-$.

The addition of t-butanol to the $Pd^{2+}/HClO_4$ system was found to significantly enhance (by a factor of about 9) the radiolytic separation yield of Pd(0). This is because of scavenging, by the addition of t-butanol, of oxidizing species arising from radiolysis of the aqueous system under study. Under these experimental conditions, the hydrogen atom is the main reducing species. Addition of chloride ions to $Pd^{2+}/HClO_4$/t-butanol system is found to completely diminish the radiolytic formation of Pd(0), due to initial formation of reduction resistant chlorocomplexes. While the addition of similar concentration of nitrate ions to the system does not modify initial state of Pd(II); hence, there is greater extent of radiolytic reduction possible in the presence of nitrate ion. However at higher $[NO_3^-]/[Pd(II)]$ molar ratio observed suppression in the radiolytic separation yield of Pd(0) is due to scavenging of reducing species by nitrate ions.

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