

Radiolysis of silver ion solutions in ethylene glycol: solvated electron and radical scavenging yields

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Abstract

The solvated electron yield in neat ethylene glycol (1,2-ethanediol), measured using pulse radiolysis, is $G(e_{\text{solv}}^-)_{10\text{ns}} = (1.7 \pm 0.2) \times 10^{-7} \text{ mol J}^{-1}$. The rate constant of the reaction of solvated electrons with silver cations is $k(e_{\text{solv}}^- + \text{Ag}^+) = (2.8 \pm 0.1) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and the absorption band maximum of Ag^0 is at 350 nm. The surface plasmon band of the silver clusters appears slowly at around 400 nm with a coalescence cascade rate constant of $2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The free silver ions do not scavenge ethylene glycol radicals.

In contrast, the γ -radiolysis reduction yield of Ag^+ into clusters is dose-dependent, changing from $G_t(\text{Ag}_n) = (2.5 \pm 0.5) \times 10^{-7} \text{ mol J}^{-1}$ at low dose to $G_{\text{max}}(\text{Ag}_n) = (7.5 \pm 0.5) \times 10^{-7} \text{ mol J}^{-1}$ at higher doses, when clusters accumulate. Silver cations adsorbed on clusters are able to scavenge the ethylene glycol radicals, which also contribute to their reduction for a part of $G_{\text{rad}} = (5.8 \pm 0.5) \times 10^{-7} \text{ mol J}^{-1}$. Considering the different ways the reducing radicals can be produced, it is concluded that they originate from the electron–cation recombination and from the cation–ethylene glycol reaction, but that the dissociation of excited states is a negligible path. The formation mechanisms of the radicals and the rate constants in ethylene glycol are compared with those in water and methanol.

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1. Introduction

Although the chemical effects of ionizing radiation on matter have been extensively studied for decades in the steady state and the pulse regimes (Tabata et al., 1991; Belloni et al., 2000; Jonah and Rao, 2001), the complexity of these effects is so great that a detailed mechanism has only been worked out for one system—water. The yields of primary transient radicals and the formation paths of molecular products have not been

completely evaluated for other systems. Indeed, most studies in these solvents were essentially devoted to the comparison of the properties and the time-dependent yield of the solvated electron (e_{solv}^-) as a probe of the influence of the physical and chemical properties of a liquid on the (e_{solv}^-) formation probability, and of the escape from recombination with the parent cation and other transients (for a review, see: Belloni and Margnier, 1989). Earlier, it was demonstrated that the radiation energy is absorbed by a system proportionally to the electron density of the various components, therefore mainly by the solvent molecules which are the most abundant. Therefore, the solutes are indirectly affected as they scavenge the primary species issued from the solvent and this specificity offers indeed the

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means for calibrating the radiolytic yields of the primary species.

We recently revisited the radiolysis of methanol (Mostafavi et al., 2002). On the basis of previous scavenger studies by pulse and steady-state radiolysis (Jha et al., 1972; Baxendale and Wardman, 1973, 1975; Hentz and Kenney-Wallace, 1974; Hunt et al., 1975; Getoff et al., 1992, 1993; Ferradini and Jay-Gerin, 1996) and of the effects that we observed in the presence of silver ions or charged clusters, which scavenge both solvated electrons and $\cdot\text{CH}_2\text{OH}/\text{CH}_3\text{O}\cdot$ radicals, we were able to complete the general scheme of the methanol radiolytic mechanism, with the yields of the various embranchments (Mostafavi et al., 2002).

The aim of this work is to apply a similar approach to the radiolysis of ethylene glycol (1,2-ethanediol) [static dielectric constant $\epsilon_s = 37$ (Maryott and Smith, 1951) and viscosity = 19 cP at 293 K], which is still less quantitatively known. The transient optical spectrum of electrons solvated in ethylene glycol has been determined by nanosecond pulse radiolysis (Sauer et al., 1965; Arai and Sauer, 1966; Dorfman and Jou, 1972; Okazaki et al., 1984) and by photodetachment of iodide (Chandrasekhar and Krebs, 2000). At 298 K, the maximum intensity is located at about 570 nm ($E_{\text{max}} = 2.18$ eV and $W_{1/2} = 1.43$ eV) and the extinction coefficient is $\epsilon(e_{\text{solv}}^-) = 1.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (Dorfman and Jou, 1972; Brodsky and Tsarevsky, 1976, 1984). Compared with those of e_{solv}^- in other polar solvents, the transition energy is rather high, as for the group of diols, and just below glycerol (1,2,3-propanetriol) (2.31 eV) (Arai and Sauer, 1966; Dorfman and Jou, 1972; Jou and Freeman, 1979). The reactivity with various solutes has been measured (Idriss-Ali and Freeman, 1984). The dynamics of the electron solvation in ethylene glycol has been recently studied by femto-second laser spectroscopy (Soroushian et al., 2004). We intend to apply our knowledge of the processes of metal cluster growth in liquids (Henglein, 1989; Belloni and Mostafavi, 2001) to measure the scavenging rate constants by Ag^+ and Ag_n^+ , and to calibrate the yields of radiolytic species in ethylene glycol.

2. Experimental

All the reagents were pure chemicals and were used as received, AgClO_4 from Aldrich, ethylene glycol and poly(vinyl pyrrolidone) (PVP) from Fluka. The polymer PVP is used as the stabilizer for silver clusters. The irradiation source was a ^{60}Co γ -facility of 3000 Ci with a maximum dose rate of 8 kGy h^{-1} . Due to the extreme sensitivity of silver atoms and small clusters to oxygen, the solutions containing silver ions were deaerated under vacuum before irradiation in a cell connected to an optical cell, in order to allow the optical spectra to be

recorded under vacuum. The optical cell in suprasil is protected by lead shielding during the γ -irradiation. The absorbance is measured immediately at the end of the irradiation. The dose amount absorbed in ethylene glycol was determined from the measurement in water by the Fricke dosimeter method and by taking into account the relative electronic density factor.

The details of the pulse radiolysis setup have been reported earlier (Belloni et al., 1983). Electron pulses of 3-ns duration were delivered by a Febetron 706 accelerator (600-keV electron energy) to samples contained in a quartz suprasil cell through a thin entrance window, 0.2 mm in thickness. The optical path length perpendicular to the electron beam was 1 cm. The dose per pulse was determined from the electronic density of the alcohol and from the initial absorbance of the hydrated electron. It was around 0.2 kGy (the concentration of e_{aq}^- at the end of the pulse was around $4\text{--}6 \times 10^{-5} \text{ mol dm}^{-3}$). The solution was saturated with pure N_2 and changed after each pulse. The absorbance of the transient species was analyzed by means of a classic xenon lamp, monochromator and photomultiplier setup connected with a transient digitizer. Four to five measurements of transient absorbance for each wavelength were performed in order to correct by averaging the pulse-to-pulse dose variation.

3. Results and discussion

3.1. γ -radiolysis of silver solutions in ethylene glycol

Silver cations are generally known to readily scavenge solvated electrons and $\text{H}\cdot$ atoms. Fig. 1 shows the γ -irradiation dose dependence of the optical absorption

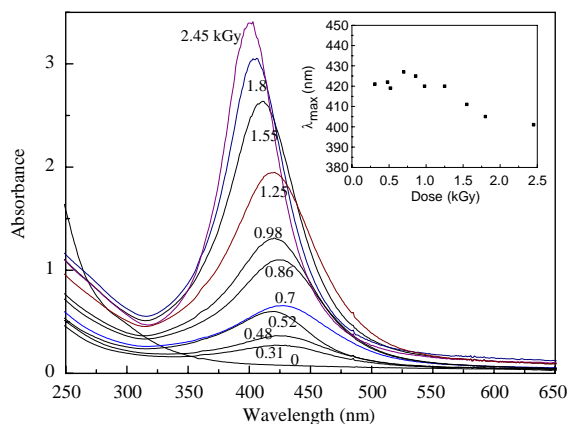
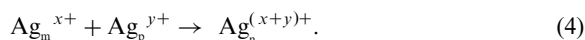
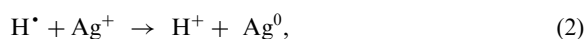


Fig. 1. Optical absorption spectra at increasing γ -dose of silver clusters in ethylene glycol. $[\text{Ag}^+] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{PVP}] = 0.1 \text{ mol dm}^{-3}$, N_2 atmosphere. Optical path: 0.1 cm. Dose rate: 2 kGy h^{-1} . Inset: shift of the wavelength of the absorption band maximum with the dose.

spectra of a solution in ethylene glycol containing AgClO_4 at $10^{-3} \text{ mol dm}^{-3}$ and PVP at 0.1 mol dm^{-3} under N_2 atmosphere. At low doses up to 1 kGy, the absorption band is of low intensity, quite broad, and displays a maximum at around 420 nm. Then, at higher doses the absorption band intensity increases and the band maximum is progressively blue-shifted to 400 nm at around 2.5 kGy (Fig. 1, inset) as it was already observed in methanol (Mostafavi et al., 2002). The absorption band corresponds to the surface plasmon band, which is specific of silver clusters and well known in different solvents (Kreibig and Vollmer, 1995). The silver clusters have been produced by the coalescence of silver atoms arising from the scavenging reaction of solvated electrons and possibly H^\bullet atoms, in so far as H^\bullet atoms are not scavenged by ethylene glycol.



Then, at 2.5 kGy the band intensity does not increase any more because the silver ions have all been reduced. The spectra are stable after the end of irradiation. The clusters are almost insensitive to oxygen, in contrast to those formed in partially reduced solutions, probably because they are smaller than at high doses. For incompletely reduced solutions, a slight increase can be observed as a very slow post-irradiation effect occurring during days. Thus, the reduction of silver ions by ethylene glycol itself, by PVP or radiolytic products during the irradiation (which lasts less than 1 h) is excluded.

Fig. 2 shows the increase in the optical absorbance at the fixed wavelength of 400 nm versus dose, and the absorbance increase at the maximum of the spectrum. Both shapes are comparable. The mean extinction coefficient per atom of silver clusters at 400 nm is derived from the absorbance value at the plateau and from the total concentration of silver atoms $n \times [(\text{Ag}_n)] = 10^{-3} \text{ mol dm}^{-3}$:

$\epsilon_{400}(\text{Ag}_n) = (1.65 \pm 0.05) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ per atom. It is worth noting that the absorbance in Fig. 2 does not increase linearly with the dose and particularly that the slope is much lower at low doses. If the same extinction coefficient is used at any dose, the average formation yield of reduced atoms at 2.5 kGy is close to $G(\text{Ag}_n) = (5 \pm 0.5) \times 10^{-7} \text{ mol J}^{-1}$. However, the initial yield is close to $G_i(\text{Ag}_n) = (2.5 \pm 0.5) \times 10^{-7} \text{ mol J}^{-1}$ (dose < 200 Gy) and the differential yield around the dose of 1 kGy is $G_{\text{max}}(\text{Ag}_n) = (7.5 \pm 0.5) \times 10^{-7} \text{ mol J}^{-1}$. Similar increases in the reduction yield versus dose curves have

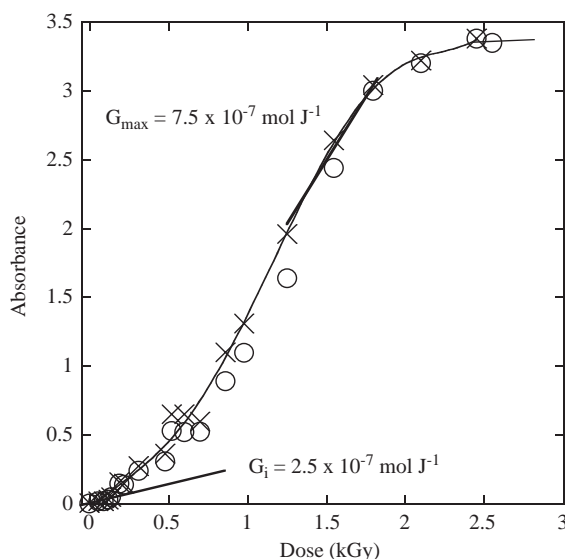
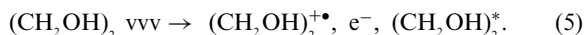


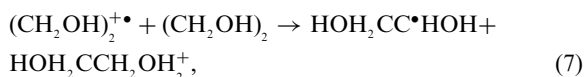
Fig. 2. Evolution with the γ -irradiation dose of the absorbance at the maximum wavelength (○) and at the fixed wavelength 400 nm (×). Same conditions as in Fig. 1.

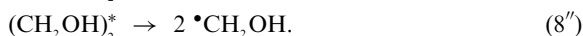
been observed in silver methanolic solutions (Mostafavi et al., 2002), where it was found that the yield is independent of the actual Ag^+ concentration, but it increases from an initial value of about $G_i(\text{Ag}_n) = (5 \pm 0.5) \times 10^{-7} \text{ mol J}^{-1}$ at low doses up to $G_{\text{max}}(\text{Ag}_n) = (12 \pm 0.5) \times 10^{-7} \text{ mol J}^{-1}$ at 1.1 kGy at total reduction. This change was assigned to the increasing concentration of silver clusters where silver cations are adsorbed and which are able to scavenge not only solvated electrons but also the alcohol radicals.

By analogy with other polar solvents, a general mechanism of the ethylene glycol radiolysis can be tentatively proposed. As in any solution, the primary effects of irradiation by the high-energy radiation are indeed the ionization and excitation of the solvent molecules of ethylene glycol [reaction (5)]:

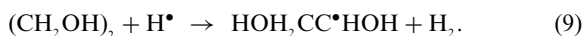


As generally accepted in the literature for polar solvents and particularly alcohols, this primary step is readily followed by the solvation of the electron, a reaction of the parent cation with another ethylene glycol molecule, yielding the radical and the protonated ethylene glycol, and the dissociation of excited states



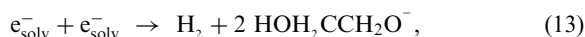
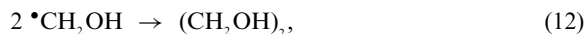
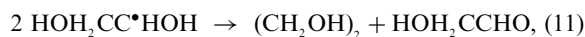
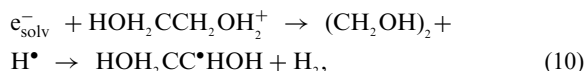


A simple loss of the excitation energy of $(\text{CH}_2\text{OH})_2^*$ during encounters with other ethylene glycol molecules is also possible. When formed by reaction (8), H^\bullet atoms are also a source of molecular hydrogen by abstracting another H^\bullet atom from an alcohol molecule, a process that occurs very early due to the high concentration (18 M) of the ethylene glycol



In water, the rate constant of the analogs of reactions (9) and (2) are $1.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively (Buxton et al., 1988). Therefore, in $2 \times 10^{-3} \text{ mol dm}^{-3}$ silver solutions, reaction (2) would represent less than 10% in the competition.

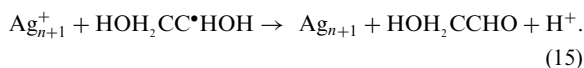
If the solvent does not contain any solute or if it is diluted, the solvated electron and other radicals react with one another and, by recombination, yield again ethylene glycol or secondary molecular products, for example



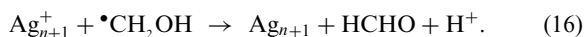
The analogs of reaction (13) are known in methanol and ethanol [$k_{13} = 3 \times 10^9$ and $5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively, according to Fletcher and Richards (1971)]. But the rate constant is much lower than that of the recombination with the cation [reaction (10)] and will be neglected in the yield estimation. The glycolaldehyde possibly formed in (8') and (11) is probably quite reactive towards (e_{solv}^-) [reaction (14)].

We suggest that in ethylene glycol the reduction yield at the highest dose is due, as in methanol or alcoholic aqueous solutions, partly to the scavenging by the silver cations of solvated electrons and partly to the scavenging by cations adsorbed on clusters of the radicals $\text{HOH}_2\text{CC}\cdot\text{HOH}$, supposed to have reducing properties as hydroxyalkyl radicals in other alcohols (Schwarz and Dodson, 1989). The redox potential of this type of radicals is more positive than that of the couple Ag^+/Ag^0 [in the range -2.1 to $-1.8 \text{ V}_{\text{NHE}}$, depending on the ligand (Remita et al., 1995; Mostafavi and Belloni, 1997)], which would exclude a direct reduction of free Ag^+ . However, a reduction of silver cations adsorbed on clusters Ag_{n+1}^+ whose potential is much more positive than that of free ions is thermodynamically possible

(Mostafavi et al., 1989; Khatouri et al., 1993). Therefore, the radicals can contribute to the reduction of adsorbed silver cations after cluster accumulation in the solution



The reduction of charged clusters by the radicals $\cdot \text{CH}_2\text{OH}$, if formed by reaction (8''), is also possible as it was postulated in the radiolysis of methanol solutions containing silver salt



The very low concentration of charged nanoclusters $[\text{Ag}_n^+]$, in the range of 10^{-8} – $10^{-7} \text{ mol dm}^{-3}$ only, explains why the radical scavenging (15–16), which is in competition with the radical disproportionation (11), is quite partial at low dose. Reactions (15) and (16) are favored at higher doses where Ag_{n+1}^+ reaches a higher concentration. Therefore, the yield at high dose is $G(\text{Ag}_n) = G(e_{\text{solv}}^-) + G(\text{HOH}_2\text{CC}\cdot\text{HOH}) + G(\cdot \text{CH}_2\text{OH}) = 7.5 \times 10^{-7} \text{ mol J}^{-1}$.

3.2. Pulse radiolysis of silver solutions in ethylene glycol

The decay of the absorbance of solvated electrons was observed first in neat ethylene glycol, then in the presence of silver ions, at 575 nm where the silver atoms do not absorb usually but Ag_2^+ absorbs slightly. The initial absorbance at 10 ns is $A_{575}(10 \text{ ns}) = 0.63$. From the dose and $\epsilon(e_{\text{solv}}^-) = 1.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (Dorfman and Jou, 1972), the solvated electron yield is determined as $G(e_{\text{solv}}^-)_{10\text{ns}} = (1.7 \pm 0.2) \times 10^{-7} \text{ mol J}^{-1}$. The e_{solv}^- decay in neat ethylene glycol is composed of a first fast part of about 150 ns, probably due to intra-spur reactions, followed by a slower homogeneous kinetics. The inset of Fig. 3 shows the decays of A_{575} at various initial concentrations of silver cations. In logarithmic scale versus time, the solvated electron decay is linear showing that the decay follows a pseudo-first-order law. Fig. 3 presents the dependence of k_{obs} on $[\text{Ag}^+]$, which is linear in the range $[\text{Ag}^+] = (0-1) \times 10^{-2} \text{ mol dm}^{-3}$ (at the lowest Ag^+ concentration, the decay is mostly due to reactions of e_{solv}^- with other radicals as in pure ethylene glycol). From the slope, the bimolecular rate constant for reaction (1) between e_{solv}^- and Ag^+ is found to be $k_1 = (3.3 \pm 0.1) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This constant is much lower than the rate constants for the same reaction in water: $3.6 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Janata et al., 1994), in liquid ammonia: $1.5 \times 10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Farhataziz et al., 1976), or in methanol: $(2.6 \pm 0.6) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Mostafavi et al., 2002). The dielectric constant of ethylene glycol ($\epsilon_s = 37$) is in the range of the values for other alcohols or ammonia. However, due to its much higher viscosity (19 cP instead of 0.55 cP for methanol and 0.145 cP for NH_3), the

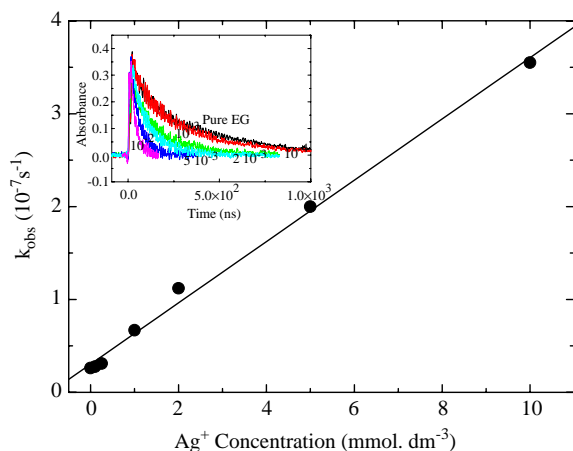


Fig. 3. Pseudo-first-order rate constant of the reaction between solvated electrons produced after a pulse in ethylene glycol and silver ions versus the silver ion concentration. Inset: decay of the absorbance at 575 nm of the solvated electron at various Ag^+ concentrations. Optical path: 1 cm. Other conditions as in Fig. 1.

mobility of all the solutes is considerably lowered. Likewise, reactions with nitrobenzene or acetone are almost ten times slower in ethylene glycol than in methanol (Idriss-Ali and Freeman, 1984).

The time evolution up to 700 ns of the transient absorbances at 575 and 350 nm of an ethylene glycol solution of $10^{-3} \text{ mol dm}^{-3}$ AgClO_4 under N_2 atmosphere is shown in Fig. 4. The increasing absorbance at 350 nm is assigned to the silver atom Ag^0 whose spectrum was studied in numerous solvents (von Pukies et al., 1968; Farhataziz et al., 1976; Mostafavi et al., 2002). During the first 100 ns, the absorbance increase at 350 nm is nearly correlated to the absorbance decay of the solvated electron at 575 nm according to reaction (1). After a maximum at around 200 ns ($A_{350, \text{max}} = 0.5$), the absorbance of Ag^0 decreases, due to reaction (3) with silver cations producing the charged dimer Ag_2^+ , which is also known in water (Janata et al., 1994), ammonia (Farhataziz et al., 1976), and methanol (Mostafavi et al., 2002). At much longer time, in the range of seconds, the progressive coalescence of silver atoms and Ag_2^+ into clusters through reaction (4) is observed at 380 nm (Fig. 5) where the maximum of the surface plasmon band of Ag_n is located. It was found in water that the extinction coefficient per atom of Ag_n increases up to $n = 13$ and is then constant (Henglein and Tausch-Treml, 1981), so that the absorbance reaches a plateau even though the coalescence continues. In ethylene glycol, the absorbance increase is achieved at around 30 s, the absorbance at the plateau being $A_{380, \text{max}} = 0.6$. Accounting for the same extinction coefficient per atom as in γ -radiolysis (Fig. 1): $\epsilon_{380}(n \times \text{Ag}_n) = 1.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$

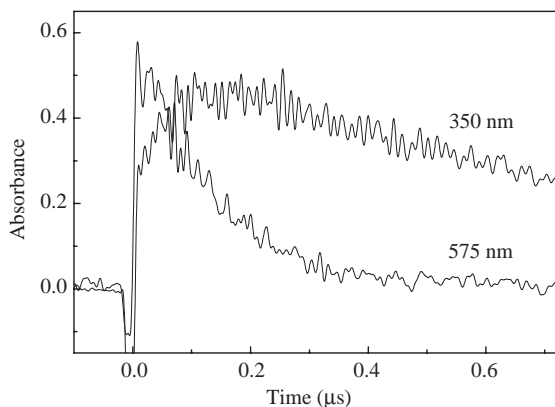


Fig. 4. Signal of the absorbance at 350 nm due to Ag^0 and of the solvated electron decay at 575 nm in the range of 0.5 μs . $[\text{Ag}^+] = 10^{-3} \text{ mol dm}^{-3}$. Other conditions as in Fig. 3.

cm^{-1} , this absorbance corresponds to a reduction yield of $G(n \times \text{Ag}_n) = 1.8 \times 10^{-7} \text{ mol J}^{-1}$. The value is close to $G(e_{\text{solv}}^-)_{10\text{ns}}$, although we noted that the electron scavenging is not complete under these conditions. Apparently, a small supplement of $(n \times \text{Ag}_n)$ is formed by the scavenging of some reducing radicals [reactions (2) and (15)].

The increase of the cluster absorbance in Fig. 5 is particularly slow compared to the same process in water (100 times) (Mostafavi et al., 1989) or methanol (7 times) (Mostafavi et al., 2002). According to the Smoluchowski coalescence model for reaction (3), the kinetics of cluster formation are independent of the conditions if the time is expressed as t/τ with $\tau = 1/k_3 \times [\text{Ag}^0]_{t=0}$, and all Ag^0 are considered as produced almost instantaneously compared to the growth. Comparing the kinetics in ethylene glycol and water, it is found that $k_3 = 2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The difference with water is partly due to the higher viscosity of ethylene glycol (20 times), but also partly to a ligandation of silver species by ethylene glycol as already noted in methanol (Mostafavi et al., 2002), or in water in the presence of CN^- ligand (de Cointet et al., 1997).

Note that in the pulse regime, the final yield of silver reduction, $G(n \times \text{Ag}_n) = 1.8 \times 10^{-7} \text{ mol J}^{-1}$, is lower than under steady-state conditions [$G(n \times \text{Ag}_n)$ up to $(7.5 \pm 0.5) \times 10^{-7} \text{ mol J}^{-1}$], a situation already observed in methanol (Mostafavi et al., 2002). In fact, the concentration of electrons and radicals is much higher after a pulse. The radical recombination (reactions (9)–(12)) is thus much faster and over before the clusters could be formed and scavenge the radicals. Therefore, the pulse radiolysis reduction yield of silver corresponds mostly to the yield of solvated electrons. In contrast, for the low dose rate γ -radiolysis, small amount of clusters are present at the lowest dose used and a part of radicals

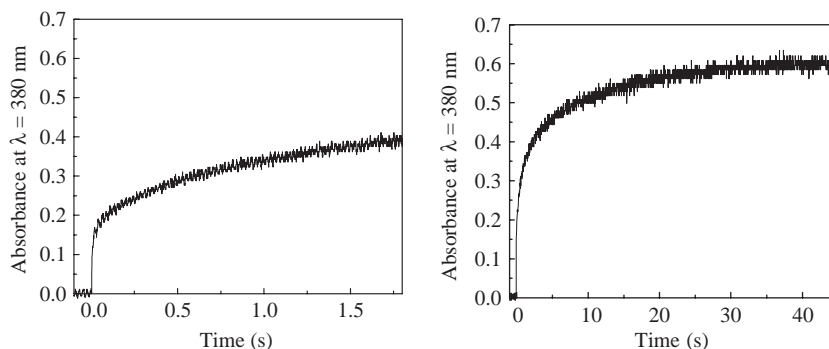


Fig. 5. Signals of the silver cluster absorbance at 380 nm in the range of 2 s (left) and 50 s (right). $[Ag^+] = 10^{-3} \text{ mol dm}^{-3}$. Other conditions as in Fig. 3.

are also used to reduce the adsorbed silver ions, so that the yield is slightly higher than in pulse radiolysis. However, at zero doses, the initial slope should be the same as in pulse radiolysis.

3.3. Yield of radicals in ethylene glycol

The yield of ethylene glycol radicals $HOH_2CC^{\bullet}HOH$ arises from the different reactions (7)–(10). The part formed in (7) is equal to the yield of the precursor $(CH_2OH)_2^{+\bullet}$ and is the same as the primary ionization yield $G(5) = G^0(\text{ionization}) = G_{e_{\text{solv}}}^0 = 4 \times 10^{-7} \text{ mol J}^{-1}$ (assumed to be the same as that found by Hunt et al. (1975) for methanol and ethanol). The radical yield arising from reaction (10) corresponds to the part of solvated electrons recombined with the parent cation, that is: $G(10) = G^0(\text{ionization}) - G(e_{\text{solv}}^-) = (4 - 1.7) \times 10^{-7} \text{ mol J}^{-1}$. The part of radicals coming from the excited states can be either the double of $G^0(\text{excitation})$ if H^{\bullet} atoms [reactions (8) and (9)] and radicals $^{\bullet}CH_2OH$ [reaction (8'')] are formed, or zero if not [reaction (8')].

According to the above mechanism (5–14) and to reactions (1) and (15), the yield of reduced silver found at high γ -dose in the presence of clusters is in the last hypothesis

$$\begin{aligned} G_{\text{max}}(n \times Ag_n) &= G(1) + G(15) = G(1) + G(7) + G(10) \\ &= G(e_{\text{solv}}^-) + G^0(\text{ionization}) \\ &\quad + [G^0(\text{ionization}) - G(e_{\text{solv}}^-)] \\ &= 2G^0(\text{ionization}). \end{aligned} \quad (17)$$

Experimentally, we found that the maximum value is $G_{\text{max}}(n \times Ag_n) = (7.5 \pm 0.5) \times 10^{-7} \text{ mol J}^{-1}$, corresponding to the complete scavenging of electrons and radicals, whereas $2 G^0(\text{ionization}) = 8 \times 10^{-7} \text{ mol J}^{-1}$. The values are close enough to conclude that the part of radicals coming from the excited states is indeed negligible, in contrast with the situation in methanol where these

radicals participate for about one third of the reduction (Mostafavi et al., 2002). Therefore, either the excited states of ethylene glycol essentially decompose into the aldehyde and molecular hydrogen by (8') without giving radicals, or geminate radicals $^{\bullet}CH_2OH$ are also formed by (8'') but their recombination by (12) is much more efficient than in methanol. Note that, in ethylene glycol as in methanol, free Ag^+ and silver ions adsorbed on clusters are reduced in γ -radiolysis by solvated electrons directly [reaction (1)], and by radicals indirectly formed in the electron recombination and in the primary cation–ethylene glycol molecule reaction [reactions (10) and (7), respectively]. Thus, this sum is equal to twice the primary ionization yield, whatever is the part of electrons scavenged. The mechanism is very similar to that of the methanol radiolysis, except that the excited states of methanol are also producing scavengeable radicals.

According to Eq. (17), the total yield of scavengeable radicals in millimolar silver solutions in ethylene glycol is $G(HOH_2CC^{\bullet}HOH) = (7.5 \pm 0.5) \times 10^{-7} \text{ mol J}^{-1} - G(e_{\text{solv}}^-)_{Ag^+} = (5.8 \pm 0.7) \times 10^{-7} \text{ mol J}^{-1}$. The various embranchments of the mechanism with the corresponding yields are summarized in the scheme of Fig. 6.

4. Conclusion

Under the conditions of γ -radiolysis and in the presence of silver clusters, the recombination of radicals is negligible, and in fact the radicals reduce the silver cations adsorbed on clusters, as they do in alcoholic aqueous solutions. The resulting total reduction yield equals the double of the ionization yield and is independent of the solvated electron yield. The γ - and pulse-radiolysis results enable us to derive quantitatively the embranchment yields of the mechanism.

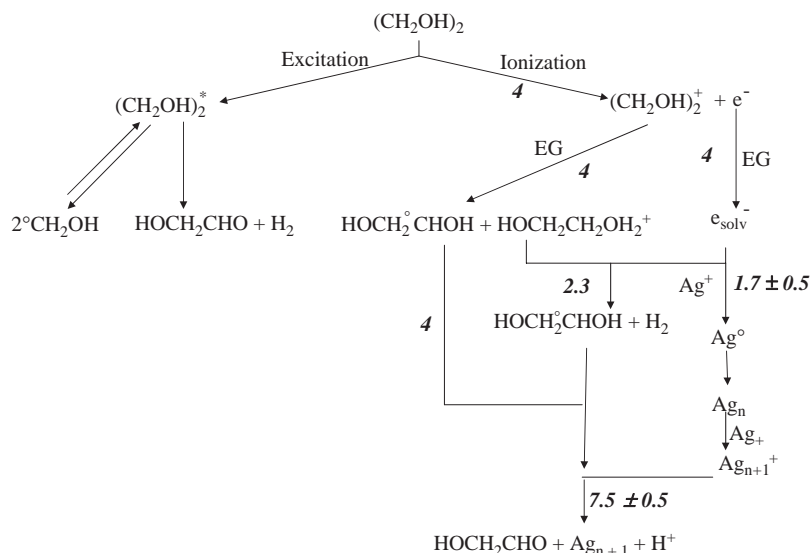


Fig. 6. General scheme of the γ -radiolysis of silver–ethylene glycol solutions. Yield values of the embranchments are given in $10^{-7} \text{ mol J}^{-1}$ unit. The species issued from the excited states do not seem to contribute to the reduction of the silver ions (see text).

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