Particle Size Effect of Silica Gel on the $\gamma$-Radiation Induced Electrical Conductivity of Urea Aqueous Solutions

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Different concentrations (0.1, 3, 6 M) of urea aqueous solutions have been irradiated with $^{60}$Co-$\gamma$-rays in the presence of silica gel (SG) of different particle size (0.1-0.5mm) at room temperature. The radiation-induced electrical conductivity (RIC) of the irradiated solutions was measured. The RIC values of the 0.1 M solutions increase as the particle size of SG decreases i.e., the particle surface area increases. This observation points to a radiation-induced chemical reactions, which are catalyzed by SG. These reactions, probably, yield products, which increase the RIC such as urea peroxide (UP). On the other hand, a different behavior was observed in the case of 3, 6 M solutions, where, the RIC increases as particle size increase. So, the mechanism of production of the species which increase the RIC of 0.1 M samples is different from that in the case of 3, 6 M. In all irradiated samples, the pH values tend to increase, slightly, as particle size increases. A mechanism was proposed to explain the obtained data.

Keywords: silica gel / urea / $\gamma$-radiation/ electrical conductivity / pH

Introduction

Generally, the radiation energy absorbed by solids dissipates into three main channels: thermal, defect formation and luminescence. In heterogeneous systems, there is a competition between surface reactions and the other energy dissipation channels. In an irradiated heterogeneous system, when the two phases each constitute a significant fraction of the total mass, the ionizing energy is absorbed significantly by both phases. When charge carriers cross from one phase to another, phenomena are thus different from those observed in a homogeneous phase. The interaction of radiation with an oxide causes electronic excitations, which promote electrons from the valence band to the conduction band, leaving holes in the valence band [1].

Since the beginning of radiation chemistry, at the end of the 19th century, much work has been conducted to determine the mechanisms of water radiolysis. Consequently, radiolysis of water [1, 2] leads to the formation of radical species (H, OH, $e^{-}_{aq}$), ions ($H_2O^{+}$, $OH^{-}$), and molecular products ($H_2O_2$, $H_2$). Water radiolysis can be written as:

$$H_2O \xrightarrow{\text{ww}} e^{-}_{aq}, OH, H, O_2H, H_2O^{+}, OH^{-}, H_2O_2, H_2$$

The radiolysis of water in contact with SG is of significant importance and is complex, where water can be strongly affected at solid/liquid interfaces, due to energy transfer from the solid to adsorbed molecules at the surface. This can be considered as radiation catalysis. It was considered that the absorption of radiation energy is partitioned between the solution and the
solid particles [3]. Hence, in irradiated SG, the energy transfers to the adsorbed molecules at the surface, by positive holes and generated electrons. Some of these reactions have been formulated to explain the chemical behavior of the irradiated SG:

\[
\text{SG} \quad \rightarrow \quad \text{SG}^\ast + e^- \quad (1)
\]

\[
\text{SG} \quad \rightarrow \quad \text{SG}^+ \quad (2)
\]

The excited electrons become available for reaction with solution species such as water (eq. 3).

\[
e^- + n \text{H}_2\text{O} \rightarrow e^-\text{aq} \quad (3)
\]

\[
\text{SG}^+ + e^- \rightarrow \text{SG}^\ast \quad (4)
\]

\[
\text{SG}^+ + e^- \rightarrow \text{SG}^{**} \quad (5)
\]

Where \(\text{SG}^\ast\) and \(\text{SG}^{**}\) stand for the excited states of SG [4]. The deposited energy in SG, crosses the solid-liquid interface and appears in the aqueous phase as solvated electrons [5]. Holes, on the other hand, remain trapped in the silica particles [6]. Moreover, pulse radiolysis experiments of aqueous suspensions of nanometer-sized silica have proven that electrons formed in the particle migrate out in the bulk water [7]. It should be mentioned that the hydrated electron is of a great importance in the development of radiation chemistry.

Radicals escaping irradiated SG surface, would diffuse and react with a solute or become distributed more uniformly [8]. Seino et al, noted that radiolytic yield of hydrogen depends on gamma radiation dose absorbed and metal oxide particle size [9, 10]. Radiolysis of urea aqueous solutions was studied before in different workers [11-16]. Urea is relatively stable to ionizing radiation in aqueous solutions up to 20 kGy [11]. Moreover, it was reported that the RIC of urea aqueous solutions significantly increases upon \(\gamma\)-radiolysis [12, 13]. This phenomenon was attributed to the UP formation [14]. The aim of the present work is to investigate the effect of SG particle size on the radiation-induced electrical conductivity (RIC) of urea aqueous solutions.

**Experimental**

Urea (98%), have been obtained from Sigma-Aldrich. SG was obtained from Merk (mesh 60-120 for chromatographic use). The different particle sizes (A= \(\leq\)0.16mm, B= \(>\)0.16mm - 0.2mm, C= \(>\)0.2mm - \(\leq\)0.5mm, D=\(\leq\)0.5mm) were obtained by sieving after washing SG by distilled water and drying at 100°C.

20 ml urea aqueous solutions (0.1, 3, 6 M), were added to 2 g of the SG with different particle sizes in 50 ml glass bottle with stopper. Irradiations were carried out in a \(^{60}\)Co \(\gamma\) - source (India Gamma chamber 4000 A, India at the NCRRT) with a dose rate of 1.25 kGy h\(^{-1}\).

**pH measurements**

Measurements were performed using an Orion Research model SA210 pH/meter. The measurements were carried out at room temperature after calibration using standard buffer solutions at pH 10.00, and pH 4.00.

**Electrical conductivity measurements**

The electrical conductivity was measured at room temperature using a Kent EIL5007 conductivity meter (Kent industrial measurements—Brown Boveri). The conductivity meter, with a cell constant of 1 cm\(^{-1}\), was calibrated using NaCl standard solutions [17]. The electrical conductivity of the irradiated solutions was measured immediately after irradiation.

Double-distilled water obtained from an all glass apparatus, was used in the preparation of the urea aqueous solutions and for final rinsing of all glass ware, its specific conductivity does not exceed 0.1 \(\mu\)S cm\(^{-1}\). Each value, in the presented results, is the average of 3 measurements.

**Result and Discussion**

When diluted aqueous solutions are irradiated, practically, all the energy absorbed is deposited in water molecules and the observed chemical changes are brought about indirectly via the formed radical products in water. Direct action of radiolysis on the solute is, generally, unimportant in dilute solutions i.e. at solute concentrations below about 10 % per weight [18]. The author of the present work suggested in a previous publication the formation of urea peroxide (UP) when urea aqueous solution is \(\gamma\)-irradiated [14]. Herein, it should be mentioned that UP increases the electrical conductivity of the medium [12, 13, 15].

Accordingly, in the present study, the observed RIC can be attributed mainly to the formation of UP and \(\text{H}_2\text{O}_2\). The effect of SG particle size on the
RIC of urea aqueous solutions were studied at different urea concentrations; 0.1, 3 and 6M.

Effect of SG particle size on the RIC of 0.1M urea aqueous solutions

It is well known that the surface area of the SG particles increases as the particle size decreases. The data in Table (1) indicate that as the particle size increases, the RIC decreases. This can be attributed to that the concentration of the species which increase the RIC, such as UP, increases as surface area of the SG particles increases. Consequently, it seems that SG enhances (catalyzes) the radiation induced formation of these species and consequently the RIC of the medium.

Generally, at 0 kGy absorbed dose, the electrical conductivity increases as the particle size increases, for all concentrations. This could be attributed to that, as particle size increases the amount of adsorbed urea on the SG surface decreases and consequently the free urea in the bulk of the solution increases. But, after irradiation the highest RIC value were observed at the smallest particle size, i.e. largest surface area. This observation points to a radiation-induced chemical reaction that occurs on the surface of SG. The products of these reactions, probably, include UP, which increases the RIC of the medium [12, 13, 15]. This observation can be explained by the electron-hole (e /h+) pairs generated in SG (eq.1) via interactions with ionizing radiation [3, 19]. It should be mentioned that UP formation in γ-irradiated urea aqueous solutions was discussed before in a previous work [14].

The released e⁻ from the irradiated SG (eq.3) will be hydrated by the silanol groups and residual water on the gel [17] (eq.3). Thus, the recombination of electron initially produced with positive holes may be suppressed [17]. Consequently, OH⁻ ions are then discharged (oxidized) by the positive holes on the oxide and as a result OH radicals are produced [20, 21]. Consequently, the yield of H₂O₂ increases (eq.6) [21,22]:

\[
2 \text{OH}^- \rightarrow \text{H}_2\text{O}_2 \quad (6)
\]

\[
\text{(H}_2\text{N})_2\text{CO} + \text{H}_2\text{O}_2 \rightleftharpoons (\text{H}_2\text{N})_2\text{CO} \bullet \text{H}_2\text{O}_2 \quad (7)
\]

So, the yield of UP will also increase (eq.7). Moreover, another mechanism was proposed for the formation of OH via the reaction of water with ³exciton (eq.8) on the surface of SG [5]:

\[
³\text{Exciton} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H} \quad (8)
\]

Therefore, the yields of OH and, consequently, H₂O₂ and UP are expected to be related to the surface area, i.e. particle size of SG. So, this surface area effect is then gradually suppressed when the size of the silica particles is increased [5].

Table (1): Effect of particle size of silica gel on the RIC (\(\mu\text{S.cm}^{-1}\)) of 0.1M urea aqueous solutions:

<table>
<thead>
<tr>
<th>Particle size</th>
<th>0 kGy</th>
<th>3.75 kGy</th>
<th>18.13 kGy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.40</td>
<td>10.80</td>
<td>15.00</td>
</tr>
<tr>
<td>B</td>
<td>1.55</td>
<td>10.50</td>
<td>14.10</td>
</tr>
<tr>
<td>C</td>
<td>4.20</td>
<td>5.40</td>
<td>09.90</td>
</tr>
<tr>
<td>D</td>
<td>0.52</td>
<td>2.70</td>
<td>11.40</td>
</tr>
</tbody>
</table>

Fig. (1): Effect of absorbed radiation dose (kGy) on the RIC (\(\mu\text{S.cm}^{-1}\)) of 0.1M urea aqueous solutions in the presence of different particle size of SG: ■ 0mm, ● \(\leq 0.16\text{mm}\), ○ \(>0.16\text{mm} - 0.2\text{mm}\), ▼\(>0.2\text{mm} - \leq 500\mu\text{m}\), ▲0 mm

It seems that SG has a dual behavior. Where, SG catalyzes the formation of products, such as UP, and H₂O₂ which enhance the RIC. On the other hand, SG adsorbs different species such as UP and H₂O₂ on its surface, which, consequently, reduce the electrical conductivity of the solution. So, in...
irradiated solutions containing the largest particle size SG i.e., the smallest surface area (>0.2mm-≤500μm), the minimum RIC value was observed. This observation can be related to the superiority of the adsorption property over the catalytic property of this particle size of SG.

Fig. (1) shows that for the 0.1M urea aqueous solutions, in the absence of SG (Δ) as well as in the presence of SG (▼,>0.2mm≤500μm), RIC increases linearly as the absorbed dose increases (0-18.13 kGy). However, at a smaller particle size of SG a nonlinear increase in the RIC was observed as the absorbed dose increases (0-18.13 kGy). This observation can be attributed to the increase of the effect of the adsorption property of SG as UP and H₂O₂ concentrations increase, at 18.13 kGy.

Table (2): Effect of particle size of silica gel on the pH of 0.1M urea aqueous solutions A=≤0.16mm, B=>0.16mm - 0.2mm, C=>0.2mm≤500μm, D=0 mm

<table>
<thead>
<tr>
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<th>0 kGy</th>
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</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.4</td>
<td>5.8</td>
<td>5.9</td>
</tr>
<tr>
<td>B</td>
<td>7.1</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>C</td>
<td>6.7</td>
<td>6.0</td>
<td>6.1</td>
</tr>
<tr>
<td>D</td>
<td>7.0</td>
<td>5.7</td>
<td>5.7</td>
</tr>
</tbody>
</table>

According to the data in Table (2), it can be considered that the pH tends to increase as the particle size of SG increases for all the studied doses (>0). This means that the concentration of the basic species increases, or acidic species decrease. It can be proposed that OH⁻ ions are discharged (oxidized) by the loss of electrons on the SG surface via +ve holes of the (e/h⁺) pairs and as a result OH radicals are produced [20]. The oxidation of OH⁻ ions by the +ve holes depends on the amount of these holes and consequently, the surface area i.e., particle size of SG. Therefore, the yield of OH⁻ ions will increase and, consequently the pH, as the particle size increases. It is apparent from Table(2) that the pH values of the irradiated samples, generally, decreases as the absorbed dose increases, at each particle size. This observation can be attributed to the radiation-induced formation of UP and H₂O₂. It is worthwhile to say that H₂O₂ decreases the pH of the medium [23]. Moreover, urea stabilizes hydrogen peroxide via formation of urea peroxide adduct [24].

Effect of SG particle size on the RIC of 3 and 6M urea aqueous solutions

The data in the Tables (3 and 5) clearly shows the increase of RIC as the absorbed doses increase for each particle size of SG for 3 and 6M urea aqueous solutions. This observation can be related to the radiation-induced formation of UP and H₂O₂ [14]. It is obvious that the magnitude of the measured RIC increases as the concentration of urea increases at the same absorbed dose and particle size. Also, the effect of SG particle sizes on the RIC at 3M and 6M is different from that of diluted solution (0.1M), where, at 3M and 6M, the RIC decreases as particle size decreases. It seems that at high urea concentrations (3 and 6 M) another mechanism is going on, beside that followed in the case of 0.1M solution. This can be attributed to the predominance of the adsorption property over the catalytic effect of SG on the formation of the species which increases the RIC. So, at 3M and 6M urea concentrations, it seems that the concentration of urea is high enough to be adsorbed on SG surface and consequently hinders the electron-hole (e/h⁺) pair mechanism, through which H₂O₂ and UP are produced, to some extent. Therefore, RIC decreased as SG surface area decreases due to decrease of the amount of H₂O₂ and UP. Also, as the particle size of SG decreases the surface area of the particle size increases, consequently, the amount of the absorbed urea, H₂O₂ and UP increases. So, the decrease in RIC, as particle size decreases, can be attributed to the decreases of both free urea, H₂O₂ and UP in the bulk of the solution.

The decrease in pH, in the case of 3 and 6M solutions, upon radiolysis can be attributed to the increase of the concentration of UP as well as H₂O₂ in the bulk of the solution, for all particle sizes (Tables 4 and 6).

Table (3): Effect of particle size of silica gel on the RIC (μS.cm⁻¹) of 3.0M urea aqueous solutions: (A=≤0.16mm, B=>0.16mm - 0.2mm, C=>0.2mm≤500μm, D=0 mm)

<table>
<thead>
<tr>
<th>Particle size</th>
<th>0 kGy</th>
<th>3.75 kGy</th>
<th>18.13 kGy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.4</td>
<td>8.1</td>
<td>19.8</td>
</tr>
<tr>
<td>B</td>
<td>4.4</td>
<td>7.8</td>
<td>19.2</td>
</tr>
<tr>
<td>C</td>
<td>5.7</td>
<td>8.85</td>
<td>21.6</td>
</tr>
<tr>
<td>D</td>
<td>5.2</td>
<td>6.79</td>
<td>10.6</td>
</tr>
</tbody>
</table>

Fig. (2): Effect of absorbed radiation dose (kGy) on the RIC (μS . cm$^{-1}$) of 3M urea aqueous solutions in the presence of different particle size of SG: ▼ >0.2mm-≤500μm, ▲ ≤0.16mm, ○ >0.16mm - 0.2mm, ● 0mm

Table (4): Effect of particle size of silica gel on the pH of 3.0M urea aqueous solutions: (A=≤0.16mm, B=>0.16mm - 0.2mm, C=>0.2mm-≤500μm, D=0 mm)

<table>
<thead>
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</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.7</td>
<td>6.3</td>
<td>6.4</td>
</tr>
<tr>
<td>B</td>
<td>6.9</td>
<td>6.3</td>
<td>6.4</td>
</tr>
<tr>
<td>C</td>
<td>7.1</td>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>D</td>
<td>7.8</td>
<td>6.0</td>
<td>5.7</td>
</tr>
</tbody>
</table>

It is worthwhile to say that the measured values of the pH after radiolysis are smaller in the case of 0.1M solutions relative to that of 3 and 6M solutions at the same dose and particle size, where, urea in 3 and 6M solutions enhance the formation of OH$^-$ ions. As the adsorbed urea on the surface of SG can react with e$^{-}_{aq}$ to form a urea anion (eq.9), the +ve hole (h$^+$) can neutralize the urea anion (eq. 10) to urea. Moreover, urea anion reacts with water producing OH$^-$ anion (eq. 11) [16].

\[
\begin{align*}
\text{H}_2\text{N-C(=O)}\text{-NH}_2 + e^{-}_{aq} & \rightarrow (\text{H}_2\text{N-C(=O)}\text{-NH}_2)^- \\
(\text{H}_2\text{N-C(=O)}\text{-NH}_2)^- + \text{SG}^+ (+\text{ve} \text{ hole}) & \rightarrow \text{H}_2\text{N-C(=O)}\text{-NH}_2 + \text{SG}^+ \\
(\text{H}_2\text{N-C(=O)}\text{-NH}_2)^- + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{N-C(=OH)-NH}_2 + \text{OH}^- 
\end{align*}
\]

(9) (10) (11)

It seems that, +ve hole (h$^+$) prefers to neutralizing the urea anion rather than OH$^-$ ions, consequently, irradiated 3 and 6M solutions are more basic relative to the irradiated 0.1M solutions.

Figures (2 and 3) show a linear relation of the absorbed radiation dose with the RIC (μS.cm$^{-1}$) of 3 and 6M urea aqueous solutions in the presence of different particle size of SG. Generally, at the same particle size and absorbed dose, RIC values increase as urea concentration increases. This effect of urea concentration can be attributed to the preferential adsorption of urea on SG [25], which will be obvious at higher concentrations (3 and 6M), which increases OH$^-$ ions concentration (eq.11 ) and consequently pH will increase as well as RIC.

Table (5): Effect of particle size of silica gel on the RIC (μS . cm$^{-1}$) of 6.0M urea aqueous solutions: A=≤0.16mm, B=>0.16mm - 0.2mm, C=>0.2mm-≤500μm, D=0 mm

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>6.6</td>
<td>10.5</td>
<td>26.7</td>
</tr>
<tr>
<td>B</td>
<td>6.8</td>
<td>10.2</td>
<td>26.4</td>
</tr>
<tr>
<td>C</td>
<td>7.0</td>
<td>11.4</td>
<td>27.3</td>
</tr>
<tr>
<td>D</td>
<td>8.2</td>
<td>9.3</td>
<td>15.3</td>
</tr>
</tbody>
</table>

Table (6): Effect of particle size of silica gel on the pH of 6.0M urea aqueous solutions: A=≤0.16mm, B=>0.16mm - 0.2mm, C=>0.2mm-≤500μm, D=0 mm

<table>
<thead>
<tr>
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<th>0 kGy</th>
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</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.8</td>
<td>6.5</td>
<td>6.8</td>
</tr>
<tr>
<td>B</td>
<td>6.9</td>
<td>6.5</td>
<td>6.8</td>
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<tr>
<td>C</td>
<td>7</td>
<td>6.6</td>
<td>6.9</td>
</tr>
<tr>
<td>D</td>
<td>8</td>
<td>6.3</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Conclusion
In the current study, the variation of the RIC and pH values of urea aqueous solution as the particle size changed was related to the surface area of the SG particles on which the products are formed. Generally, in all the studied samples, the magnitude of RIC values increases after radiolysis. This observation can be attributed to the increase of the yield of H$_2$O$_2$ and consequently UP, beside other ionic species. It can be concluded that the effect of the particle size of SG on the RIC of 0.1M urea aqueous solution is different from that of 3 and 6M, where, at 0.1M urea aqueous solution, the RIC decreased as the particle size of silica gel increases. So, it seems that SG enhances the radiation-induced formation of species, such as H$_2$O$_2$ and UP, consequently the RIC of the medium increases. Such observation can be related to the radiation-induced formation of electron-hole (e$^-$/h$^+$) pairs on SG surface. It should be mentioned that OH$^-$ ions are oxidized by the +Ve holes and as a result OH radicals are produced, consequently, the yields of H$_2$O$_2$ and UP increase, as well as, the RIC of the solutions. On the other hand, at 3M and 6M, the RIC decreases as particle size decreases. Therefore, it seems that in 3 and 6 M solutions, another mechanism is going on, beside that followed in the case of 0.1M solution. This can be attributed to the predominance of the adsorption property over the catalytic effect of SG. At 3M and 6M urea concentrations, it seems that the concentration of urea is high enough to be adsorbed on SG surface and consequently it hinders the electron-hole (e$^-$/h$^+$) pair mechanism, through which H$_2$O$_2$ and UP are produced, to some extent. Also, as the particle size of SG decreases (surface area increases) the amount of the absorbed urea, H$_2$O$_2$ and UP increases. Consequently, RIC decreases due to the decrease of the concentration of free urea, H$_2$O$_2$ and UP in the bulk of the solution.

In general, the decrease in pH, in all cases, upon radiolysis can be attributed to the increase of the concentration of UP as well as H$_2$O$_2$ in the bulk of the solution. It is worthwhile to say that the measured values of the pH after radiolysis are smaller in the case of 0.1M solutions relative to that of 3 and 6M solutions at the same dose, where urea in 3 and 6M solutions enhances the formation of OH$^-$ ions. Moreover, at such high urea concentration, the oxidation of OH$^-$ ions by +ve holes is hindered by the adsorbed urea on SG surface. The magnitude of the pH values increases as the particle size of silica gel increases for most of the studied samples, where, the formation of acidic products (UP and H$_2$O$_2$) is related to the +ve holes formed on the surface area of SG.

Acknowledgments
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