Opportunities for improving the performance of LCV micelle gel dosimeters: I. Preliminary investigation

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Abstract. The effects of the various components of leuco crystal violet (LCV) micelle gels on dose sensitivity and initial colour are tested. Dose sensitivity and gel turbidity are influenced by tri-chloro acetic acid (TCAA) concentration, with the highest dose sensitivity obtained at ~21.5 mM. Increasing Triton x-100 (Tx100) concentration improved dose sensitivity but, unfortunately, increased initial colour of the gel. Using Cetyl Trimethyl Ammonium Bromide (CTAB) in place of Tx100 produces gels that are nearly colourless prior to irradiation, but reduces the dose sensitivity. The effects of chlorinated species on dose sensitivity are tested using 2,2,2-trichloroethanol (TCE), chloroform, and 1,1,1-trichloro-2-methyl-2-propanol hemihydrate (TCMPH). TCE gives the largest improvement in dose sensitivity and is recommended for use in micelle gel dosimeters because it is less volatile and safer to use than chloroform. A new gel containing CTAB as the surfactant and TCE gives improved dose sensitivity compared to previous LCV micelle gels.

1. Introduction

Radiochromic micelle gel dosimeters, developed by Jordan and co-workers for optical readout, are promising because they have the potential to produce accurate 3D dosimetry results [1] with excellent spatial stability [2-4]. However, current micelle gel dosimeters have relatively lower dose sensitivity compared to Fricke gel dosimeters [3]. Leuco dye micelle gels are also sensitive to temperature during irradiation and are sensitive to light exposure during storage [2, 3]. Among the two radiochromic micelle gels developed by Jordan and co-workers, LCV micelle gels are recommended over leuco malachite green (LMG) micelle gels because the LCV gel dosimeters exhibited linear dose response, lower effective diffusion, and higher dose sensitivity [3]. The recommended LCV micelle gel recipe reported by Babic et al [3] contains five components: 4.0 wt% gelatin, 4.0 mM Tx100 surfactant, 25.0 mM TCAA, 1.0 mM LCV, and ~96.0 wt% water. This recipe is referred to as Jordan’s standard LCV gel throughout this article. To develop this recipe, Babic et al [3] studied the effects of varying the concentrations of Tx100, LC, and TCAA on dose sensitivity. They found that dose sensitivity could be improved by increasing Tx100 concentration. They also showed that a concentration of ~25.0 mM TCAA maximizes the dose sensitivity. The influence of TCAA on dose sensitivity may arise from two factors, which were discussed by Vandecasteele et al [4]: TCAA contains chlorine atoms that may have a sensitizing effect and is an acid that influences pH.

Vandecasteele et al [4] reported difficulties in making LCV micelle gels using Tx100 and replaced it with sodium dodecyl sulfate (SDS). When attempting to make radiochromic micelle gels using...
diacetylenes as reporter molecules, Nasr et al [5] tested Tx100, SDS and CTAB as surfactants. Precipitation problems were observed for several diacetylene gels produced using Tx100 and SDS, while transparent stable gels were obtained using CTAB. Vandecasteele et al [4] also studied the effect of adding chloroform to LMG micelle gels (made with SDS) and reported an improvement in dose sensitivity. This result is not surprising because chloroform is an important component used in some PRESAGE gels [6, 7] and chloroform and other chlorinated molecules are effective in increasing dose sensitivity in other dosimetry applications, due to a variety of chemical reactions [8].

The purpose of the current study is to gain a deeper understanding of the effects of various gel components on dose sensitivity, initial colour prior to irradiation, and gel transparency of LCV micelle gels. First, the effect of TCAA concentration on dose sensitivity and gel transparency is studied. Next, the effect of surfactant type and concentration on dose sensitivity and initial colour is studied using Tx100 and CTAB. Finally, the effects of three halogenated hydrocarbons (chloroform, TCE and TCMPH) on dose sensitivity are investigated.

2. Materials and Methods

2.1. Gel preparation, irradiation, and scanning

The following manufacturing procedure was followed to manufacture gels:

1- Add gelatin (Type A, 300 Bloom porcine skin) into 75 wt% of the total deionized water in the recipe and let swell for 20 minutes. Then stir while heating to 45 °C until gelatin dissolves.

2- Add surfactant (Tx100 or CTAB) and TCAA to the remaining 25 wt% of the deionized water and stir at room temperature for 5 minutes until dissolved.

3- Add LCV to the mixture from step 2 and stir at room temperature for 5 minutes.

4- Pour LCV mixture from step 3 (at room temperature) into gelatin mixture from step 1 (at 45 °C) and stir for 2 minutes.

Samples of the final mixture, produced using a variety of recipes, were poured into 4.5 ml polystyrene cuvettes with 10 mm light path and sealed using a cap and Parafilm. pH was measured using a pH electrode. All gels were refrigerated at 4 °C for ~24 h and then placed in a water bath at 22 °C for 20 minutes before irradiation. A Varian Clinac 6EX linear accelerator was used to irradiate the cuvettes to different doses of 0, 5, 10, 15, 20, and 40 Gy at a dose rate of 400 cGy min⁻¹. Absorption spectra were measured ~20 minutes after irradiation using a SpectroVis Plus spectrophotometer over the wavelength region of 380-900 nm. Absorbance measurements were calibrated using a reference cuvette filled with deionized water. Further details are provided in [9].

2.2. Effect of TCAA concentration on dose sensitivity and gel transparency

Gels were made with different TCAA concentrations of 14.5, 21.5, 25.0, 27.5, and 33.5 mM. Gelatin and Tx100 concentrations were fixed at 4.0 wt% and 4.0 mM, respectively (as in Jordan’s standard LCV gel) and the LCV concentration was fixed at 0.25 mM.

2.3. Effect of surfactant type and concentration on dose sensitivity of LCV micelle gels

Gels were manufactured using Tx100 (4.0, 19.0, and 39.0 mM) and CTAB (at 2.5, 9.0, and 17.0 mM). TCAA, LCV, and gelatin concentrations were fixed at 25.0 mM, 1.0 mM, and 4.0 wt%, respectively.

2.4. Effect of halogenated species on dose sensitivity of LCV micelle gels

Chloroform, TCE, and TCMPH were tested as chlorinated additives to improve dose sensitivity of LCV micelle gels. TCE and TCMPH were selected because of their lower volatility and lower toxicity compared to chloroform. LCV micelle gels were made at two different concentrations (10.0 and 90.0 mM) of each of the three chlorinated species. All gels were manufactured as described in section 2.1 except that, in step 2, the halogenated compound was added to the surfactant and TCAA solution and mixed for ~10 minutes before LCV was added. Concentrations of gelatin, Tx100, LCV and TCAA were kept at 4.0 wt%, 4.0 mM, 1.0 mM, and 25.0 mM, respectively as in Jordan’s standard LCV gel.
An additional gel was produced using 60 mM TCE in a gel where Tx100 was replaced by 17.0 mM CTAB.

3. Results and Discussion

3.1. Effect of acid concentrations (pH) on dose sensitivity and gel transparency

Results in table 1 show that TCAA strongly influences dose sensitivity in a nonlinear fashion, with the highest dose sensitivity obtained at a TCAA concentration of 21.5 mM (gel 1.3). A similar maximum in dose sensitivity was observed by Babic et al [3]. LCV micelle gels manufactured at low acid concentration (high pH) were turbid (gels 1.1, 1.2). This result reveals that the transparency of LCV micelle gels is influenced by acid concentration (or pH).

Table 1. Dose sensitivity of LCV micelle gels at different concentrations of TCAA. Concentrations of gelatin, LCV, and Tx100 were fixed at 4 wt%, 0.25 mM, and 4 mM, respectively. Absorbance values were measured at 590 nm.

| #  | TCAA Conc. [mM] | LCV [mM] | Transparency | Initial Colour | Initial Absorbance | Dose Sensitivity [Gy⁻¹.cm⁻¹] | pH  |
|----|----------------|----------|--------------|----------------|--------------------|-------------------------------|-----|
| 1.1| 14.5           | 0.25     | Turbid       | ----           | 0.185              | 3.87·10⁻³                   | 4.04|
| 1.2| 18.0           | 0.25     | Turbid       | ----           | 0.122              | 5.37·10⁻³                   | 3.75|
| 1.3| 21.5           | 0.25     | Clear        | No             | 0.030              | 6.38·10⁻³                   | 3.63|
| 1.4| 23.0           | 0.25     | Clear        | Light Blue     | 0.036              | 5.64·10⁻³                   | 3.43|
| 1.5| 25.0           | 0.25     | Clear        | No             | 0.030              | 4.79·10⁻³                   | 3.36|
| 1.6| 27.5           | 0.25     | Clear        | No             | 0.019              | 4.33·10⁻³                   | 3.15|
| 1.7| 33.5           | 0.25     | Clear        | No             | 0.018              | 1.93·10⁻³                   | 2.63|

3.2. Effect of surfactant type and concentration on dose sensitivity and initial colour

The dose sensitivity of LCV gels increased with increasing Tx100 concentration, as shown in table 2. Unfortunately, the initial colour of the un-irradiated gels also increased with increasing Tx100. Using CTAB at different concentrations resulted in gels with no noticeable initial colour, but did not improve the dose sensitivity. Similar gels prepared using SDS at different concentrations (not shown) resulted in viscous, turbid and sticky mixtures that are not suitable for optical scanning [9].

Table 2. Dose sensitivity of LCV micelle gels made using Tx100 and CTAB. Surfactant concentrations were selected so that the number of micelles/L in the gels would be roughly 1, 5.5, and 10 times the number of micelles in Jordan’s standard LCV gel. Gelatin, TCAA, and LCV concentrations were fixed at 4.0 wt%, 25 mM, and 1.0 mM, respectively. Gel 2.2 is a replicate of Jordan’s standard LCV gel. Absorbance values were measured at 590 nm.

| #  | Surfactant | Conc. [mM] | Transparency | Initial Colour | Initial Absorbance | Dose Sensitivity [Gy⁻¹.cm⁻¹] | pH  |
|----|------------|------------|--------------|----------------|--------------------|-------------------------------|-----|
| 2.1| --         | 4.0        | clear        | No             | 0.020              | 5.50·10⁻³                   | 3.40|
| 2.2| Tx100      | 4.0        | clear        | Light Blue     | 0.049              | 7.65·10⁻³                   | 3.36|
| 2.3| Tx100      | 19.0       | clear        | Dark Blue      | 0.116              | 1.09·10⁻²                   | 3.44|
| 2.4| Tx100      | 38.0       | clear        | Dark Blue      | 0.207              | 1.37·10⁻²                   | 3.43|
| 2.5| CTAB       | 2.5        | clear        | No             | 0.020              | 5.62·10⁻³                   | 3.37|
| 2.6| CTAB       | 9.0        | clear        | No             | 0.025              | 5.57·10⁻³                   | 3.39|
| 2.7| CTAB       | 17.0       | clear        | No             | 0.026              | 5.80·10⁻³                   | 3.39|

3.3. Effect of halogenated hydrocarbons on dose sensitivity of LCV micelle gels

Results in table 3 show that dose sensitivities of LCV micelle gels were highest for gels containing TCE. Moreover, the dose sensitivity of LCV micelle gels increased with increasing TCE concentration. Using chloroform did not affect the dose sensitivity of LCV micelle gels significantly compared to gel (3.7) which is a standard Jordan LCV gel. When TCMPH was used at the low concentration of 10.0 mM, dose sensitivity was higher than that of Jordan’s standard LCV gel.
However, when the TCMPH concentration increased to 90.0 mM, dose sensitivity decreased below that of Jordan’s standard LCV gel.

Gel (3.8), which contained 60.0 mM TCE and 17.0 mM CTAB (in place of Tx100) was colourless and had the highest dose sensitivity of any gel in this study, except for gels (2.3) and (2.4), which were dark blue prior to irradiation. TCE will be used as a gel additive in our on-going research because it gives the best dose sensitivity results of the three additives tested.

Table 3. Effects of adding three different halogenated compounds on dose sensitivity of LCV micelle gels. Concentrations of LCV, TCAA, Tx100 and gelatin are the same as in Jordan’s standard LCV gel, except for Gel 3.8, which contains 17.0 mM CTAB in place of Tx100. Gel 3.7 is a replicate of Jordan’s standard LCV gel. Absorbance values were measured at 590 nm.

| #  | Halogenated hydrocarbon | Conc. [mM] | Transparency | Initial Colour | Initial Absorbance | Dose Sensitivity [Gy⁻¹.cm⁻¹] | pH   |
|----|-------------------------|------------|--------------|----------------|--------------------|-----------------------------|------|
| 3.1| Chloroform              | 10.0       | Clear        | Light Blue     | 0.048              | 8.08·10⁻³                   | 3.40 |
| 3.2| Chloroform              | 90.0       | Clear        | Light Blue     | 0.017              | 7.09·10⁻³                   | 3.34 |
| 3.3| TCE                     | 10.0       | Clear        | Light Blue     | 0.054              | 9.07·10⁻³                   | 3.34 |
| 3.4| TCE                     | 90.0       | Clear        | Light Blue     | 0.088              | 1.25·10⁻²                   | 3.39 |
| 3.5| TCMPH                   | 10.0       | Clear        | Light Blue     | 0.055              | 9.26·10⁻³                   | 3.42 |
| 3.6| TCMPH                   | 90.0       | Clear        | Light Blue     | 0.041              | 7.32·10⁻³                   | 3.43 |
| 3.7| ----                    | ----       | Clear        | Light Blue     | 0.055              | 7.74·10⁻³                   | 3.48 |
| 3.8| TCE                     | 60         | Clear        | No             | 0.030              | 9.37·10⁻³                   | 3.29 |

4. Conclusions
This study was conducted to gain a deeper understanding of the effects of various components in LCV micelle gels on dose sensitivity, initial colour, and gel transparency. A maximum in the dose sensitivity vs. TCAA response curve is obtained using ~21.5 mM TCAA. Turbid gels are produced when a low concentration of TCAA (≤18.0 mM) is used. Dose sensitivity increases with increasing Tx100 concentration but, unfortunately, the initial colour of the un-irradiated gels also increases, which may cause complications during optical scanning in larger containers. Using CTAB to replace Tx100 surfactant produced colourless gels prior to irradiation, but reduced dose sensitivity (by ~26%) when no chlorinated species (except TCAA) are included in the recipe. The effects of three halogenated compounds (chloroform, TCE and TCMPH) on dose sensitivity were tested. TCE is the most effective at improving the dose sensitivity and is safer to use than chloroform because it is less volatile and less toxic. Using this information, a new gel is proposed using CTAB as the surfactant and TCE as a sensitizer. This new gel has improved dose sensitivity compared to that in Jordan’s standard LCV gel, and has no noticeable colour prior to irradiation. Additional information is provided elsewhere [9].

5. References
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