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Radiolytic formation of Ag clusters in aqueous polyvinyl alcohol solution and hydrogel matrix

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Abstract

Ag^+ ions, in aqueous polyvinyl alcohol (PVA) solution and in PVA hydrogel matrix have been gamma radiolytically reduced to produce Ag clusters. UV-visible absorption spectral characteristics of Ag clusters obtained under different gamma dose, Ag^+ concentration, PVA concentration and crosslinking density of the gel used have been studied. The effect of Ag^+ ions on the radiation crosslinking of the PVA chains, have also been investigated by viscosity measurements. The radiation-induced Ag^+ ion reduction was followed by crosslinking of the PVA chains. PVA was found to be a very efficient stabilizer to prevent aggregation of Ag clusters. The clusters produced in the hydrogel matrix were expected to be smaller than the pore size (~2–20 nm) of the gels used in the study. These Ag clusters were unable to reduce methyl viologen (MV^{2+}) chloride and were stable in air.

Keywords: Ag clusters; γ-radiolysis; Polyvinyl alcohol; Hydrogel; Crosslinking

1. Introduction

Small metal clusters are of great interest because of their nonlinear optical and special catalytic properties. Radiolytic reduction of aqueous metal ions is a simple, clean, important and one of the extensively studied techniques, for producing homogeneous colloidal dispersions of small metal particles (Michaelis and Henglein, 1992; Mostafavi et al., 1990, 1993; Mulvaney and Henglein, 1990; Ershov et al., 1991, 1992; Khatouri et al., 1992; Ershov et al., 1992; Kapoor et al., 1997; Kumar, 2002). Radiolytic reduction of Ag^+ ions in the aqueous medium is one of the most exhaustively studied systems among the different reported metal ions. Various transient intermediates such as Ag^0, Ag_2^+, Ag_3^{2+}, Ag_4^{2+}, etc. have been characterized by the technique of pulse radiolysis, and it finally results in larger Ag clusters with development of plasmon absorption band at about 380–400 nm (Henglein, 1995; Janata et al., 1994; Janata, 2003).

Similar to the colloidal solutions, the hydrogels containing metal nanoparticles, can also play an important role in catalysis of many important chemical reactions in aqueous medium. But not much work has been reported so far on the radiolytic formation of metal clusters in the hydrogel matrix. The higher stability of a catalyst in gel matrix; uniform distribution without aggregation of small clusters; easy separation of a gel-immobilized catalyst from reaction mixture; easy

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accessibility of its large surface area and its repetitive usability, are some of the main advantages offered by such hydrogel systems.

In the present work, the radiolytic formation of Ag clusters in aqueous polyvinyl alcohol (PVA) solution and PVA hydrogel, have been investigated and the two systems have been compared. The effect of Ag^+ ions on the radiation-induced crosslinking of PVA chains, has also been studied.

2. Experimental

$AgNO_3$ (E. Merck) and PVA (SD fine chemicals) having molecular weight of ~125 000 were used. Methyl viologen (MV^{2+}) chloride was from Aldrich. All other chemicals used were of GR or AnalaR grade and were used as received. Water purified with a nanopure system (conductivity < 0.1 μS/cm) was used. High-purity Iolar grade N_2 and N_2O gases were from Indian Oxygen Ltd.

Camspec-M350 spectrophotometer was used to record UV-visible spectra. Generally, the N_2 gas bubbling of aqueous solutions containing PVA in small cuvette results in loss of solution. To overcome this problem, aqueous solutions of PVA containing $AgNO_3$, were prepared using autoclave (15 psi, 121 °C), which on irradiation gave results similar to deaerated sample. The resultant clusters were found to be stable in air. Autoclaving results in partial removal of air from the solution. Therefore, for experiments, the solutions prepared by autoclaving were sealed in air-tight containers and then irradiated for graded radiation doses at room temperature. The reduction of methyl viologen (MV^{2+}) chloride to its radical cation $MV^{\bullet +}$, was tested by addition of about more than two times the required estimated amount of MV^{2+} to the respective sols under N_2-atmosphere. Aqueous 5% PVA solution was pre-irradiated for different gamma doses (15.8–72.0 kGy), to form gels with different crosslinking densities. These gels were equilibrated with excess $AgNO_3$ solution for about 20 h under N_2 atmosphere and irradiated to different gamma doses to produce Ag nanoparticles in the hydrogel matrix. Gamma irradiation was performed with a Co^{60} source (dose rate 0.5 kGy/h).

2.1. Viscosity

Viscosity measurements were carried out using an Ubbelhode type of viscometer, at 27 ± 1 °C. The specific viscosity [η_{sp}], with respect to aqueous 5% PVA solution, was calculated for different gamma-irradiated solutions containing PVA and $AgNO_3$, using the relation

$$[\eta_{sp}] = (t - t_0)/t_0, \quad (1)$$

where t_0 and t are the time of flow in the viscometer for the unirradiated aqueous 5% PVA solution and the different gamma-irradiated solutions, respectively.

2.2. Gel fraction

The gel fraction of the hydrogel samples were determined by soxhlet extraction. About 1 g of the hydrogels was extracted with water (6 h) to remove the soluble fraction. The samples were removed and dried in an air oven at 70 °C till constant weight was obtained. The gel % was calculated as

$$\text{Gel } \% = W_g/W_0 \times 100, \quad (2)$$

where W_g is the weight of dry gel after extraction and W_0 is the initial weight of the dry gel.

2.3. Equilibrium degree of swelling (EDS)

The degree of swelling was determined gravimetrically. The gels (dried to constant weight) were equilibrated for about 14 h with excess of water at room temperature and it was weighed after the surface water was removed with a filter paper. The EDS was calculated as

$$\text{EDS} = (W_e - W_i)/W_i, \quad (3)$$

where W_e is the equilibrium weight of the hydrogel and W_i is the initial weight of the dried gel.

3. Results and discussion

The radiation crosslinking of PVA molecules is known to be induced mainly by OH radicals in aqueous medium (Ulanski et al., 1994).

$$PVA(H) + {}^{\bullet}OH \rightarrow PVA^{\bullet} + H_2O \quad (4)$$

$$2\ PVA^{\bullet} \rightarrow PVA—PVA \text{ (crosslinked polymer)} \quad (5)$$

Resulting in a three-dimensional network of the hydrogel. Ag^+ ions are known to have very high reactivity with both hydrated electrons ($k = 4.8 \times 10^{10}$ $dm^3\,mol^{-1}\,s^{-1}$) and hydroxyl radicals ($k = 9.7 \times 10^9\,dm^3\,mol^{-1}\,s^{-1}$) (Ershov et al., 1993; Bonifacic et al., 1991). Whereas, under the present experimental conditions, the hydroxyl radicals almost exclusively react with PVA and the reduction of Ag^+ ions takes place both by strongly reducing hydrated electrons and the polymeric radicals $PVA^{\bullet}$ (having structure similar to alcohol radicals) formed by H atom abstraction reaction from PVA chains by hydroxyl radicals.

$$nAg^+ + e^-_{aq}/PVA^{\bullet} \rightarrow (Ag)_n \text{ (Ag clusters)} \quad (6)$$

Gamma radiolysis of N_2O-saturated aqueous solution containing $2 \times 10^{-4}\,mol\,dm^{-3}$ $AgNO_3$ and 5% PVA,