Magnetic and fluorescence properties of cobalt implanted hydrogels

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Abstract. Co-doped plain gels (PAAm) were prepared with and without pyranine fluoroprobe (8-hydroxypyrene-1, 3,6-trisulfonic acid, trisodium salt; POH), which have a OH⁻ reactive group and three SO₃⁻ ionic groups. Magnetization and fluorescence measurements were used for characterization of the gels. It was observed that both the plain gel itself and the gel including only POH (PAAm-POH) have a diamagnetic response to the external field. When the gels were synthesized together with cobalt (PAAm-Co) and cobalt/POH (PAAm-Co-POH), both gels magnetized in the direction of the magnetic field, as expected. However, the magnitude of the magnetization was different in the gels which were synthesized in the presence of POH and the one into which POH molecules were diffused after the synthesis, even though they have the same cobalt concentration. Fluorescence measurements and SEM micrographs were used to understand this surprising difference in the magnetization of PAAm-Co-POH gels. It was proposed that the electrostatic interaction between SO₃⁻ groups of POH and free electrons of cobalt (Co²⁺) atoms led to the formation of Co-POH clusters having fewer unpaired electrons, and this results in a decrease in overall magnetization. It was also observed from the SEM images that the size of clusters depends on the Co-POH composition.

1. Introduction

The synthesis of hydrogels which are sensitive to external stimuli like pH, temperature, light intensity and magnetic field have become an interesting subject of study. These gels may have applications in medicine, drug-delivery, bio-sensors, etc.[1,2] More recently, dual response polymers like pH/thermo, thermal/magnetic and pH/magnetic have been developed to increase the number of possible applications [3-7].

Hydrogels which are sensitive to magnetic fields can be synthesized by introducing ferro- [8,9] or paramagnetic [10] nanoparticles either during the gelation or by diffusing them into previously formed gels. Magnetic gels, especially ferrogels which include ferromagnetic particles, are typical examples of smart materials for mechanical actuators and the subject of many studies in recent years. For

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instance, it was also reported that hydrogels cross-linked by paramagnetic ions can be used as colorimetric pH sensors or used to remove organic materials from aqueous solution [10].

In our work, cobalt particles were embedded in hydrogels during the gelation and pyranine (POH) was used as a fluoroprobe which can be used for monitoring gelation, phase transitions and the fractal nature of the gels [11]. Magnetic and fluorescence measurements together with SEM images were used to characterize the magnetic hydrogels.

2. Experimental

The PAAm gels were synthesized as described in Ref [16]. The gels prepared with Co, PAAm-Co gels (sample 2), were prepared for two different concentrations of Co(II) acetate, 10^{-3} M, and 0.3 M. The gels prepared with POH, PAAm-POH gels (sample 3), were prepared with 10^{-4} M concentration of POH. The gels prepared with both Co and POH, PAAm-Co-POH gels (sample 4), were prepared with two different concentration of Co(II) acetate, 10^{-3} M (sample 4L), 0.3 M (sample 4H), and 10^{-4} M POH for each sample.

Once prepared, the four types of gels were divided into three different groups and the first one used without washing, the second and the third ones were washed with pure and high pH water (pH=11), respectively. Then, samples, 1, 2, and 4, were swelled in sufficient amounts of pure water and the sample 2 was swelled in similar way in 10^{-4} M POH solution (10^{-4} M POH dissolved in pure water, sample 2D) to bring them to certain swelling ratios.

The fluorescence spectra of the gels were recorded by using a charged-coupled-device (CCD) array camera (Ocean Optics USB2000) [12]. The fluorescence measurements were carried out at a 90° angle. POH molecules were excited at a wavelength of 400 nm. Magnetic measurements were performed by using a SQUID magnetometer (Quantum Design, MPMS XL).

3. Results and Discussion

3.1. Magnetic Characterization of the gels

Magnetization measurements, performed at several different applied fields but only two of them were included here, of the samples 1, 2, 3 and 4 were shown in Fig.1a as a function of increasing mass ratio, m/m_0. Here, m represents the mass after swelling and m_0 is the initial mass (i.e. dry mass) of the gels. The swelling process was performed in such a way that the diffusion of both POH molecules and Co-atoms were prevented. It was observed from the figure that the plain gel, PAAm, and the gel including POH, PAAm-POH have a diamagnetic response to the applied field and it increases with increasing water content (i.e. swelling ratio) which is also diamagnetic [13]. The magnetic behavior of Co-doped samples appeared to be more interesting, in that they have different positive magnetic moments despite both gels (2 and 4) having the same cobalt concentration. In order to understand this surprising result, we performed fluorescence measurements and used SEM images which were taken from the surface of the gels.
3.2. Fluorescence Measurements

The fluorescence spectra of PAAm-Co-POH gels (sample 4) in the collapsed and swollen states and the one which was washed with high pH water, are presented in Fig2. Almost no fluorescence intensity was observed for the gel including high Co content (4H), but the intensity became considerable for the gel including low Co content (4L) in the collapsed state (Fig. 2a). When these gels were swelled with sufficient water (pH=6), the fluorescence intensity became apparent for 4H and it increased for the gel 4L (Fig. 2b). The peak around 435 nm corresponds to the POH molecules which are chemically bonded to the PAAm strands, and the other peak around 500 nm (broad peak) is the superposition of the fluorescence peaks of free (515 nm) and excimer forms (480 nm) of POH molecules, details of which can be found in Ref. [14].

Fig.2c corresponds to the fluorescence spectra of samples 4H and 4L after washing with high pH (pH=11) water. The intensity disappears almost completely for the sample 4H; in contrast, there is no significant change for the sample 4L except for some decrease in the 515 nm side of the broad peak.
which is due to the diffusion of free POH molecules out of the gel. The same results were found when the gels were washed with pure water. The peak around 480 nm which becomes apparent after washing indicates that POH molecules did not leave the gel. The fluorescence spectra presented in Fig.2c were also supported by the magnetization measurements performed in these gels, which were washed with high pH water and then brought to the collapsed state, in the following way. The change in the magnetization of these samples after washing was completely different from each other, ~0% for sample 4L and ~86% for 4H. This observation clearly shows that the Co atoms in sample 4H were washed out of the gel together with the POH molecules during the washing process.

![Fluorescence Spectra (a.u.)](image)

**Figure 2.** Swelling and washing effect on the fluorescence spectra of POH in the PAAm gel with Co

### 3.3. Microstructure of the gels: SEM Micrographs

SEM images of the samples 2, 4 and 2D (POH diffused) in the collapsed state are shown in Fig3; these images were taken from the non-magnetized samples. In other words, no magnetic field was applied before the SEM analysis. Cobalt clusters are formed in all PAAm gels, however the mechanism of the formation is quite different in samples 2 and 4. In sample 2, Co-atoms are connected by ponderamotive forces, while in sample 4 it is the electrostatic interaction between the empty electronic states of Co atoms and the free electrons of SO$_3$ groups in POH molecules which keeps the Co-atoms and POH molecules together. SEM-EDX analysis showed that these big and small clusters include Co-atoms which can not be due to the magnetic interactions, since magnetic fields were not applied either during the synthesis or the SEM analysis.
The average size of these cobalt clusters depends on the composition of Co and POH. Synthesizing the composites in the presence of Co and POH together (sample 4) gave the largest average cluster size, ~5600 ± 500 nm. In addition, the density of these clusters is higher than the others formed in the composites prepared without POH. If the composites are synthesized with only Co, the average size of the clusters decreases to ~1550 ± 260 nm. When the POH molecules are diffused into previously formed PAAm-Co gel (2D), the average size surprisingly gets smaller than that of the others.

![SEM micrographs of samples 2 (a) and (b), 4 (c) and 2D (d) in collapsed states.](image)

**Figure 3.** SEM micrographs of samples 2 (a) and (b), 4 (c) and 2D (d) in collapsed states.

In summary, our results showed that synthesis of the gel together with POH molecules results in stable and large clusters between Co and POH molecules via only ionic interactions, i.e. electrostatic interactions. The cluster formation with Co atoms and POH molecules can occur only during the polymerization and these clusters can not be created by the magnetic interactions between the Co-atoms, since there was no applied field during the synthesis. In other words, Co-atoms were not magnetized during the synthesis which may cause an attractive interaction. When the POH molecules were diffused into the PAAm-Co gel after the preparation, no change in the magnetization was observed. They behave like flocculants and decrease the average size of the Co clusters dispersing them via attractive electrostatic interactions. Therefore, the stability and size of Co clusters formed in the gel composites are controlled by the anionic agents, POH.
4. References

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