Effect of Eu(III) chloride on the gelification behavior of poly(acrylic acid)

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Supramolecular gels are an important class of soft materials: they are basically formed by solvent molecules inside in a 3D network structure and can be considered from soft and weak to hard and tough, depending on their mechanical properties. [1] The gelation process can be accomplished in different ways through, for example, interaction between a charged polymer and a metal ion. [2]

In this work, the interaction between poly(acrylic acid) (PAA) and the trivalent ion Eu(III), to form luminescent gels, has been studied.

For that, a phase diagram for polymer-ion mixture has been plotted (Figure 1) showing that for high molar ratios Eu3+/PAA different phase transitions take place. We have focused our work in the region where the formation of weak and strong gels is occurring.

From rheological measurements, we have found that the mechanical strength of gels increases by increasing the concentration of PAA, because the elastic module (G') increases when it increases the concentration of PAA. A similar trend is found in yield stress values, from which the gel begins to behave as a liquid. Thus, the higher the concentration of PAA the higher the yield stress. The frequency sweeps shows that PAA-Eu gels and weak gels exhibit a rheological solid-type behavior, with a storage module (G') predominating over loss modulus (G'') in the studied frequency.

The formation of the gel phase can also be followed by fluorescence spectroscopy. It can be observed that the emission of fluorescence at 424 nm increases by increasing the molar ratio Eu3+/PAA. Such behavior may be explained both by a decrease in the number of coordinated water molecules and by binding of Eu(III) to deprotonated PAA. However, the formation of gel phase is reversible and dependent on the Eu(III) concentration; in fact, by increasing the molar ratio values, above a certain critical point, it occurs a disaggregation of the gel structure, mainly due to electrostatic repulsions between ions Eu(III) and Eu3+/PAA; this is supported by the decrease in the emission of fluorescence of Eu(III) mixed solutions. The effect of Eu(III) in the PAA gel formation mechanism is complemented with the analysis of FTIR, SEM and EDX mapping data.

Fig. 1. Phase diagram of Eu3+/PAA mixed system.

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