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Molecular interactions in polyacrylamide/lithium perchlorate hydrogel composites

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Abstract

In this study, the effects of introduction of lithium perchlorate into polyacrylamide hydrogels having constant amounts of acrylamide monomers and N,N'-methylene-bis-acrylamide crosslinker have been studied through the observed changes in the vibrational Raman spectra. The changes in the perchlorate anion's Raman modes show that in the polymeric matrix most of the lithium and perchlorate ions are separated by the polyacrylamide coils. The changes in the Raman modes of the polymeric chains show that the interactions of the two ionic species with the coils are unfavourable to the hydrogen-bond network of the hydrogel matrix. As the amount of lithium perchlorate in the hydrogel increases the role played by the intra and inter-molecular hydrogen bonds due either to the amide groups or the interstitial water decreases; the amide groups become more accessible to chemical transformations and the hydrogel flexibility increases. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyacrylamide composites; Polymer ionic association; Raman spectroscopy

1. Introduction

In the last decades, polymer solid electrolytes have attracted considerable attention, especially in the fields of polymer chemistry and physics, solid-state electrochemistry and energy storage technology [1]. Various methods have been applied to modify the structure and morphology of the host matrixes of these polymers in order to improve their electrolyte characteristics. One of the successful approaches has been to prepare composite network polymers containing high polar organic or inorganic fillers additives for lowering the polymer host crystallinity and flexibility [2,3]. Little is known about the mechanisms responsible for the observed changes of the crystallinity and the flexibility of the polymer host upon the addition of such additives. Recently, in the case of composite polymers with alkali metal salts, these changes have been explained as resulting from acid/base interactions involving either the metal cations or the anions with the acid/base centres of the polymer [4]. The strength of the interactions between the added salts in polymer electrolytes and the polymer host, in comparison with that of the interionic forces is, at present one of the serious problems with current theories on this kind of system [5].

Vibrational studies are known to be very useful to analyse this kind of ion–ion interaction in polymeric electrolytes [6,7]. Using perchlorates as additives, the position and shape of the characteristic vibrational bands of the perchlorate anion have been analysed in detail.

Using lithium perchlorate as a model electrolyte dissolved in a polyacrylamide matrix hydrogel, the present work examines the effects of addition by reporting the observed changes in the vibrational features of the perchlorate anion and the polyacrylamide chain and the interstitial water molecules as a function of the concentration of additive, at 295 K.

2. Experimental

Lithium perchlorate/polyacrylamide composites were prepared according to the following procedure: constant monomer acrylamide, N,N'-methylene-bis-acrylamide and agar–agar aqueous solutions were prepared by dissolving: 0.375 g of acrylamide for synthesis (Merck), 0.0075 g of N,N'-methylene-bis-acrylamide (Sigma, reagent grade) and 0.075 g of agar–agar for analysis (Montplet & Esteban SA), respectively, in 5 ml of distilled water. Each solution was mixed until visible dissolution of the solid components. This was followed by the addition to each solution of stoichiometric amounts of anhydrous lithium perchlorate

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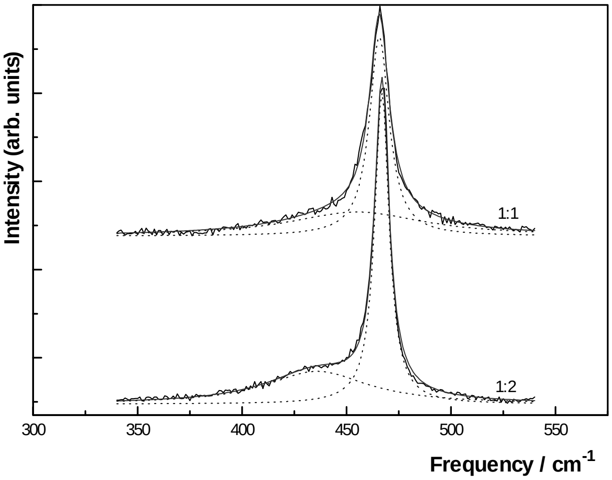

Fig. 1. The perchlorate anion A_1 Raman bending, at 295 K, for polyacrylamide/lithium perchlorate hydrogel composites containing 1:1 and 1:2 mol of acrylamide to lithium perchlorate.

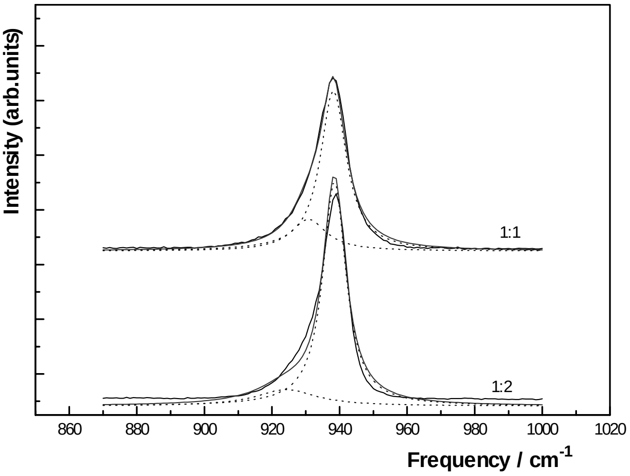

Fig. 3. The perchlorate anion A_1 Raman stretching, at 295 K, for polyacrylamide/lithium perchlorate hydrogel composites containing 1:1 and 1:2 mol of acrylamide to lithium perchlorate.

(Fluka AG. Buchs SG), in order to obtain composite polymers having acrylamide to lithium perchlorate molar ratios in the range 1:1 to 1:2. After about half an hour of mixing, 3–4 drops of hydrogen peroxide were added to the solution, acting as an initiator for the polymerization reaction. The mixture was placed in an oven at ~80°C until the gelation process started to occur (ca. 1.5 h). The temperature was then reduced to about 60°C and the samples were kept at this temperature for a few hours. The amount of water included in each sample after the drying process was calculated on the basis of gravimetric measurements and was observed to be 6–8% which corresponds to about 1:1 water to acrylamide molar ratio [8].

The Raman spectra were recorded on a Ramalog double spectrometer, 0.85 m, f/7.8, Spex model 1403, equipped with holographic gratings with 1800 grooves/mm, The light source used as Raman excitation was the 514.5 nm line of an argon ion laser (Coherent, model Innova 90). The instrumental resolution was limited to 1 cm^{-1}. A detector assembly containing a Hamamatsu type R928 photomultiplier tube, for 190–860 nm, multi alkali, in thermoelectric cooled housing, was used for detection. Raman data were stored on disk, with the possibility of further processing. The error in wavenumbers is estimated to be within ca. 1 cm^{-1}.

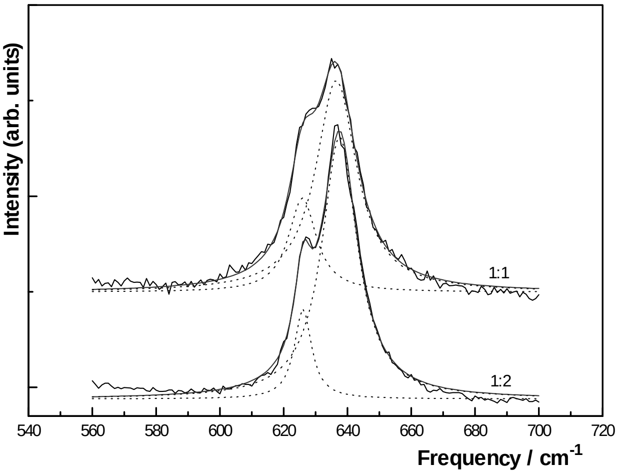

Fig. 2. The perchlorate anion E Raman bending, at 295 K, for polyacrylamide/lithium perchlorate hydrogel composites containing 1:1 and 1:2 mol of acrylamide to lithium perchlorate.

3. Results and discussion

3.1. The perchlorate anion vibrational modes

Figs. 1–3 show the two lorentzian fittings of the perchlorate anion Raman bendings and stretching, at 295 K, for polyacrylamide/lithium perchlorate composite hydrogels containing 1:1 and 1:2 moles of acrylamide to lithium perchlorate.

The curve fitting shows that the band envelope corresponding to each of the three perchlorate ion modes may be separated into two contributions. The lower frequency component is attributed to “spectroscopically free” perchlorate anions, whereas the higher frequency component can be associated with the presence of contact-ion pairs. Under this assumption, the fraction of free anions and contact-ion pairs can be calculated from the ratio of the areas under the two components. The spectroscopically free perchlorate anions correspond to solvent-separated ion pairs $Li^+\cdots ClO_4^-$ and solvent separated dimers of the type

$$\begin{array}{l} Li^+\cdots ClO_4^- \\ ClO_4^-\cdots Li^+ \end{array}$$

whereas the bound or contact species of perchlorate anion correspond to lithium perchlorate species where the lithium cation is separated from the perchlorate anion by the polyacrylamide coils [7].

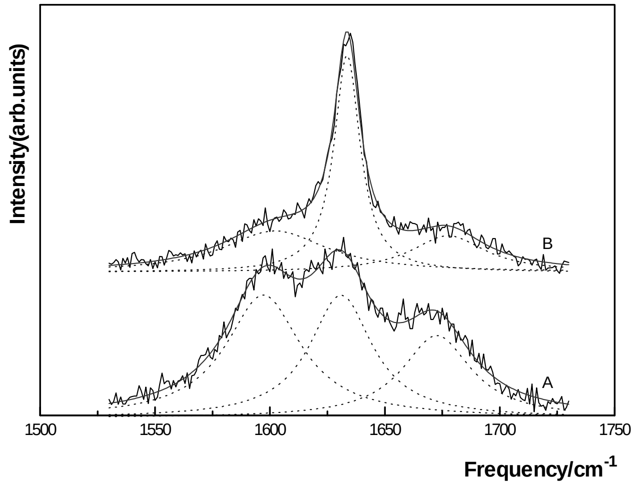

Fig. 4. The C=O Raman vibrational stretching region, at 295 K, for: (A) polyacrylamide hydrogel matrix; and (B) polyacrylamide/lithium perchlorate 1:2 hydrogel composite.

Following this interpretation, in the studied polyacrylamide/lithium perchlorate composite hydrogels, the peak characteristics for bound or contact species is much larger than the corresponding "free" anions, i.e. the majority of the perchlorate anions in the hydrogel exists out of contact with the lithium ions. And, as expected from a presumed equilibrium between separated ion pairs ↔ contact species, from all the three modes, a decrease in the order of 6–10% in the amount of free anions is calculated with the increasing concentration of lithium perchlorate in the composite from 1:1 to 1:2 moles of acrylamide to additive.

3.2. Bands originating from the amide I vibrational mode

Fig. 4 shows the 1530–1730 cm^{-1} Raman vibrational region for the polyacrylamide hydrogel matrix and the polyacrylamide/$LiClO_4$ hydrogel composite containing 1:2 moles of acrylamide to lithium perchlorate, at 295 K. The bands in this region correspond to the so-called amide I vibrational mode, the C=O stretching [9]. Clearly, it is possible to divide the registered band envelope in this region into three individual peaks that fit quite well to three lorentzian functions centred around 1597, 1630 and 1670 cm^{-1}. A great amount of self-association of acrylamide in the polyacrylamide hydrogel matrix through hydrogen bonding under the experimental conditions is expected. The water content of the hydrogel (less than 10%) is not sufficient to prevent such a self-association. Two kinds of self-association have been proposed for amides: one is a linear hydrogen bonding between a hydrogen atom of a NH_2 group and an oxygen atom of a carbonyl group of another molecule; the other is a closed dimer formed by two hydrogens bonds as in carboxylic acids [10]. According to studies of the C=O stretching modes for different amides hydration states, the component at ca. 1630 cm^{-1} should correspond to the C=O stretching mode of a non self-associated amide molecule, whereas the modes at around 1597 and 1672 cm^{-1} should correspond to the stretching of the carbonyl group in the associated amide [11]. There is an increase of the component at ca. 1630 cm^{-1} with regard to the other two C=O stretching components upon adding lithium perchlorate to the polyacrylamide hydrogel matrix. In the case of the 1:2 mol of acrylamide/lithium perchlorate composite shown in Fig. 4, the increase of non self-associated amide, as calculated from the components area, goes from ca. 34 to 44.8%. It is well known that in aqueous solutions, the perchlorate anion produces an extensive breakdown of the hydrogen-bonded water structure similar to the breakdown resulting from a large temperature rise [12]. And it is also known that Li^+ enters into specific interactions with the amide groups [13] with a split of hydrogen bonds involving the carbonyl groups. The observed spectral features correspond to a decrease of the amount of hydrogen bonds in the polymeric structure of the composite.

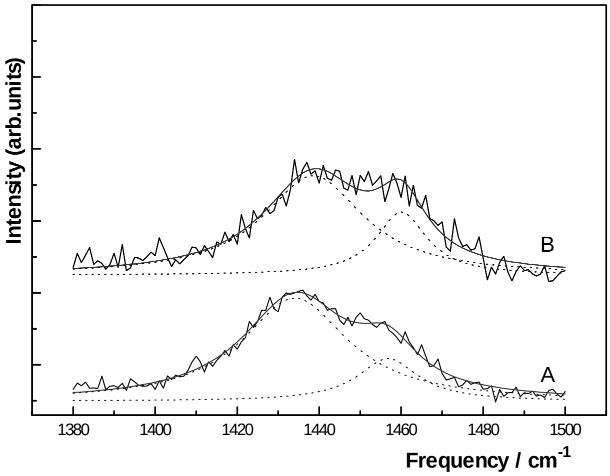

Fig. 5. The C–N Raman vibrational stretching region, at 295 K, for: (A) polyacrylamide hydrogel matrix; and (B) polyacrylamide/lithium perchlorate 1:2 hydrogel composite.

3.3. Bands originating from the amide III vibrational mode and the CH_2 bending

Fig. 5 shows the Raman 1380 to 1500 cm^{-1} spectral region, at 295 K, for the studied polyacrylamide hydrogel matrix and a 1:2 mol of acrylamide to lithium perchlorate hydrogel composite. In this region, the band at 1434 cm^{-1} is assigned to the amide III mode, the C–N stretching, and the band at 1456 cm^{-1} to the CH_2 bending for the A species [14]. On adding lithium perchlorate to the hydrogel, the frequency of the two vibrational modes is unaffected, but there is a significant increase in the intensity of the CH_2 bending mode relative to the C–N stretching. In the hydrogel matrix, the intensity of the bending mode is about 24% of the CH_2 bending intensity, whereas in the case of the 1:2 hydrogel composite such intensity is more than 32% of the peak at 1434 cm^{-1}. This change can be explained as being a result of the conformational changes in the polyacrylamide

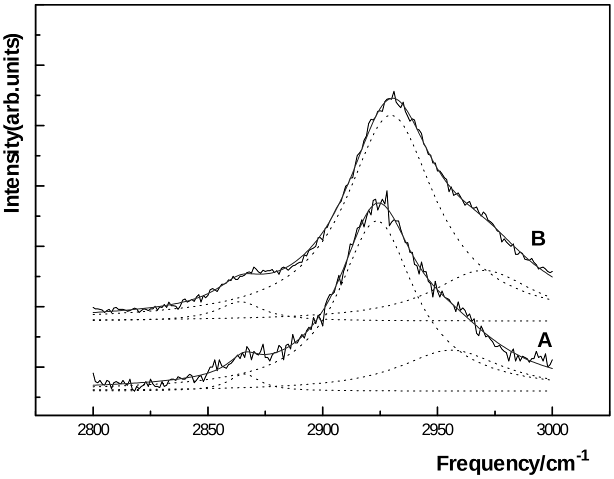

Fig. 6. The C–H Raman vibrational stretching region, at 295 K, for: (A) polyacrylamide hydrogel matrix; and (B) polyacrylamide/lithium perchlorate 1:2 hydrogel composite.

chain because of the molecular interactions with the additive.

3.4. The C–H stretching vibrational region

The observed Raman bands in the C–H Raman vibrational region for the studied polyacrylamide hydrogel, at 295 K, occur at 2865, 2923 and 2955 cm^{-1}. Clearly, these frequencies are very close to those of the CH stretching vibrations of solid polyacrylamide, with the CH stretching vibration at 2867 cm^{-1}, the symmetric CH_2 stretch at 2931 cm^{-1} and the asymmetric CH_2 stretch at 2960 cm^{-1}, respectively and quite different from those of acrylamide in aqueous solution [15,16]. There are no changes in the C–H stretching on adding lithium perchlorate to the hydrogel; but, there is a significant increase in the frequencies of the CH_2 stretches, ca. 7 cm^{-1} for the symmetric mode and ~15 cm^{-1} for the asymmetric mode (Fig. 6). The effect of the lithium perchlorate on the splitting of hydrogen bonds explains these changes in frequency as much as the polyacrylamide CH_2 groups are involved in the whole hydrogen-bonding network.

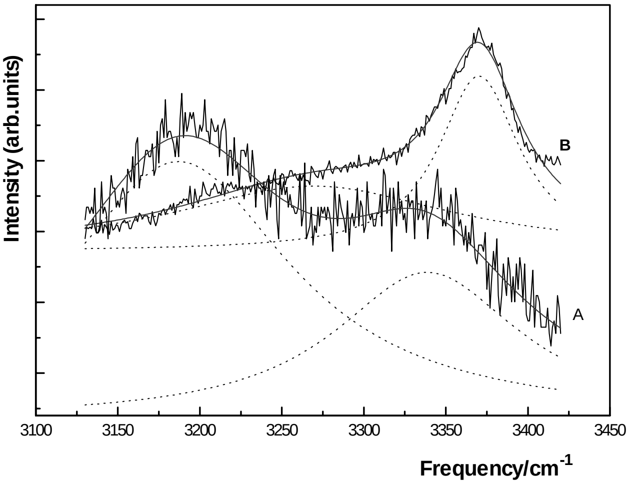

Fig. 7. The water O–H Raman vibrational stretching region, at 295 K, for: (A) polyacrylamide hydrogel matrix; and (B) polyacrylamide/lithium perchlorate 1:2 hydrogel composite.

3.5. The water O–H Raman vibrational stretching

The Raman O–H stretching vibration of the interstitial water in the studied polyacrylamide hydrogels was observed in the region 3100 –3400 cm^{-1}, consisting of a combination of two broad components (Fig. 7). For the polyacrylamide hydrogel matrix, these two components are centered at about 3187 and 3338 cm^{-1}, respectively, where, following Green et al.'s studies [17], the lower-frequency component should be assigned to a collective in-phase stretching of hydrogen-bonded O–H, whereas the higher–frequency component would correspond to the stretching of the non-bonded O–H oscillators. The collective band has been observed to displace by a few cm^{-1} to lower frequencies as the temperature decreases allowing a more intense coupling between O–H···O–H oscillators [16,18]. The "associated" water molecules around the polyacrylamide chains, owing to hydrophilic interactions, are restricted in their molecular motions compared to those in pure water [19]. The greater the water association through effective O–H···O–H coupling, the weaker the O–H stretching.

Introduction of the structure breaking perchlorate anion into the hydrogel, inducing the already mentioned structural and topological changes in the hydrogen-bonded network of the polymeric polyacrylamide species, reduces the effective coupling between the interstitial water molecules; thus, the number of associated O–H···O–H oscillators decreases as the amount of additive increases and the remaining association is significantly weakened. This is a clear conclusion from the observed increase in the frequency of the two O–H stretching components with a great increase in the intensity of the higher-frequency component relative to the intensity of the lower-frequency component.

4. Conclusion

The perturbation of the crystalline structure of polyacrylamide hydrogels due to the introduction of lithium perchlorate salt into the polymer is evident both from the changes in the perchlorate anion vibrational modes and the changes in the vibrational modes sensitive to the polymer backbone conformation. The perchlorate anion spectral features in polyacrylamide/lithium perchlorate hydrogel composites indicate that in these composites the majority of the perchlorate anions are not in contact with the lithium ions; most of the ionic species in the composites are contact species consisting of lithium cation separated from the perchlorate anion by the polyacrylamide coils. From the polyacrylamide spectral features, one concludes that these coils form cross-links by hydrogen bonding with small water domains. The counterions of the lithium perchlorate salt used as an additive to the polyacrylamide hydrogel strongly disturb the hydrogen-bond network of both the polymer and the interstitial water, owing to the specific interactions of the lithium ion with the amide groups and the structural breakdown due to the perchlorate anion. Thus, as the amount of lithium perchlorate in the polyacrylamide matrix increases amide groups become more accessible with an increase in the hydrogel flexibility.

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