

CONDUCTIVITY RELAXATION OF POLY(ETHYLENE OXIDE)/CUSO₄ SOLID SOLUTION

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Introduction

When polymers are mixed together with alkali metal salts, the resulting complex is referred as an electrolyte polymer. The polymer matrix involved in this kind of systems must be capable of dissolving the salt which can dissociate giving place to an ionic conductivity. During the last decades the interest for polymer electrolytes has been increased due to its potential technological applications, specially in the construction of electrochemical devices such as sensors, batteries and fuel cells. The more suitable polymer in this context is poly(ethylene oxide), PEO, which has been subjected to a wide range of research particularly its complex with lithium salts. In this contribution we are reporting a dielectric study on solid solution formed by poly(ethylene oxide) into which has been dissolved weighed amount of copper sulfate.

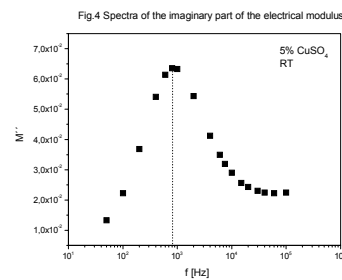
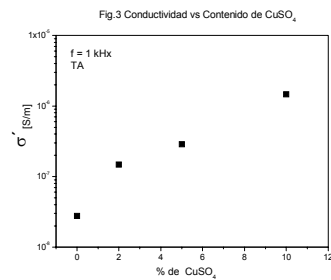
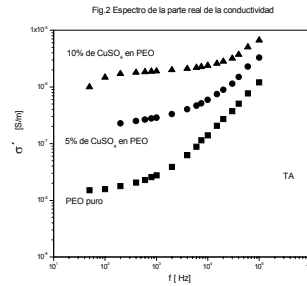
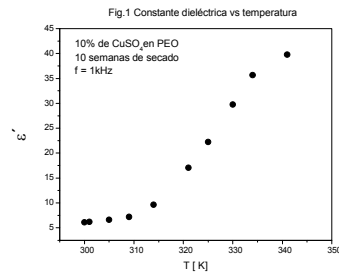
Experimental details

Poly(ethylene oxide) used in this study was supplied by Aldrich Chemical with a molecular weight of 3×10^5 and copper sulfate by Kodak, CO. The mixture was prepared by dissolving weighed amounts of CuSO₄ in proportion from 5% to 10% by weight of PEO, in distilled water. Once the components were dissolved, the solution was casted over a pyrex glass substrates and kept there during one hour at room temperature; then the substrates were placed into a vacuum oven at 30 °C for two days, and films 20 μm thick were obtained. The films were subjected to a further drying from one to ten weeks at RT. Films above 10% in content of CuSO₄ became brightless and presented poor mechanical stability, so they were rejected. For measurement, the films were sandwiched between two stainless steel electrodes forming samples with parallel plates capacitor structure. The dielectric response was obtained with the help of a digital capacitance bridge General Radio model 1689. The temperature was monitored by a thermocouple chromel-alumel connected to a digital thermometer digi-sense model 8528-40.

Results and Discussion

Figure 1 shows the dielectric constant for a typical sample 10 % of CuSO₄ by weight of PEO, at

a function of temperature and frequency of 1 kHz. It was observed an increase of the dielectric constant by increasing temperature, which is an evidence that the process involved corresponds to an ionic relaxation conductivity, so the real part of the ionic conductivity was estimated through the relation $\sigma'(\omega) = \epsilon_0 \epsilon'' \omega$, where ϵ'' is the dielectric loss and ω the angular frequency. Fig.2 shows the spectrum of $\sigma'(\omega)$ for samples with different contents of CuSO_4 at room temperature; we can observe, at the same time, a decrease of conductivity by decreasing frequency with a tendency to reach a stable value at very low frequencies which can be identified with a dc ionic conductivity (σ_{dc}) and an increase with the content of CuSO_4 . Fig. 3 depicts the behaviour of $\sigma'(\omega)$ with the content of CuSO_4 at a frequency of 1 kHz, it is observed a tendency to a saturation level for contents above 10% of CuSO_4 in PEO. We can estimate the value of the dc ionic conductivity using the complex electrical modulus (M^*). In this context, a plots of M'' (imaginary part of M^*) vs f (linear frequency), when $\sigma_{dc}/\epsilon_0 \omega \gg \epsilon''(\omega)$, must be show a peak at a frequency f_0 given by $\sigma_{dc}/2\pi\epsilon_0\epsilon_s$, where ϵ_s is the low frequency limited dielectric constant. In plots of this kind, very well defined peaks were observed for all concentration of CuSO_4 as shown in fig.4, from which values of dc ionic conductivity were obtained in the range from 1.4×10^{-6} S/m at 5% of CuSO_4 to 3.3×10^{-5} S/m at 10% of CuSO_4



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