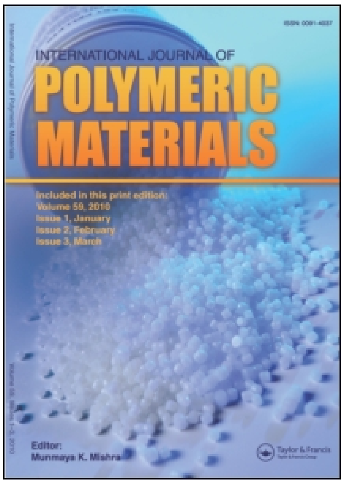

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Conductivity Studies of Poly(ethylene oxide)/Copper Sulfate Solid Solutions

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ac and dc electrical conductivities of solid solutions of poly(ethylene oxide) (PEO) and copper sulfate ($CuSO_4$) had been obtained from dielectric measurements as a function of temperature, frequency of applied electric field, and content of salt between 2% and 12% of $CuSO_4$ by weight of PEO. The behavior of the dielectric constant with temperature showed evidence that the observed dielectric response was due mainly to migration of ions. The dielectric response was analyzed in the frame of the complex electrical modulus, from which it was possible to estimate values of dc ionic conductivity from $3{,}81 \times 10^{-7}$ S/m for a content of 2% of salt to $5{,}5 \times 10^{-6}$ S/m for a content of salt of 12% at room temperature, indicating an increase of the electrical conductivity by increasing the content of $CuSO_4$. The behavior of ionic conductivity with temperature was compatible with the free volume model through the Volmer, Tamman, and Fulcher empirical equation. These preliminary experimental results allowed the conclusion that an electrolyte polymer has been prepared with base in poly(ethylene oxide)/copper sulfate mixtures, with a higher ionic conductivity in the order of $5{,}5 \times 10^{-6}$ S/m at room temperature.

Keywords: Ionic conductivity; Complex electrical modulus; Free volume; Complex dielectric function

INTRODUCTION

When polymers are mixed together with alkali metal salts, the resulting complex is called an electrolyte polymer [1–3]. The polymer matrix involved in this kind of systems must be capable of dissolving the salt that can dissociate and give rise to an ionic conductivity. During the

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Address correspondence to Simón Santos, Avenida Universidad, Cerro Colorado, Cumaná Código Postal 6101, Venezuela. E-mail: ssantos@sucre.udo.edu.ve last decades the interest in polymer electrolytes has increased due to their potential technological applications, especially in the construction of electrochemical devises such as sensors, batteries, and fuel cells. The more suitable polymer in this context has been poly(ethylene oxide), PEO [4], which has been subjected to a wide range of research, particularly its complexes with lithium salts [5–6]. This contribution reports ionic conductivity measurements obtained from a dielectric study on solid solution formed by poly(ethylene oxide) in which there has been dissolved weighed amounts of copper sulfate ($CuSO_4$).

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 $CuSO_4$ in proportion from 2% to 12% by weight of PEO, in distillate water. Once the components were dissolved, the solution was cast over Pyrex glass substrates and kept at rest for one hour at room temperature; then the substrates were placed in a vacuum oven at 30°C for two days, and films 20 μm thick were obtained. The films were subjected to further drying from one to ten weeks at room temperature in order to extract residual water. Films above 12% in content of $CuSO_4$ became brittle and presented poor mechanical stability, so they were rejected. For measurements, the films were sandwiched between two stainless steel electrodes forming samples with parallel plates capacitor structure and placed in a homemade sample holder. The structure was connected to a digital capacitance bridge General Radio model 1689. The dielectric response was obtained as a function of frequency of the applied electric field, temperature, and content of $CuSO_4$. The temperature was monitored by a cromel-alumel thermocouple connected to a digital thermometer Digi-sense model 8528-40.

EXPERIMENTAL RESULTS

Figure 1 shows the spectrum of the dielectric constant at room temperature for typical sample 5% of $CuSO_4$ by weight of PEO, obtained after further drying of one week and ten weeks, respectively. It is observed that the dielectric constant decreases by increasing the time of drying, which is an evidence of a decrease of the water content in the sample under test, consequently all the experimental results reported in this work correspond to samples subjected at least ten weeks of further drying.

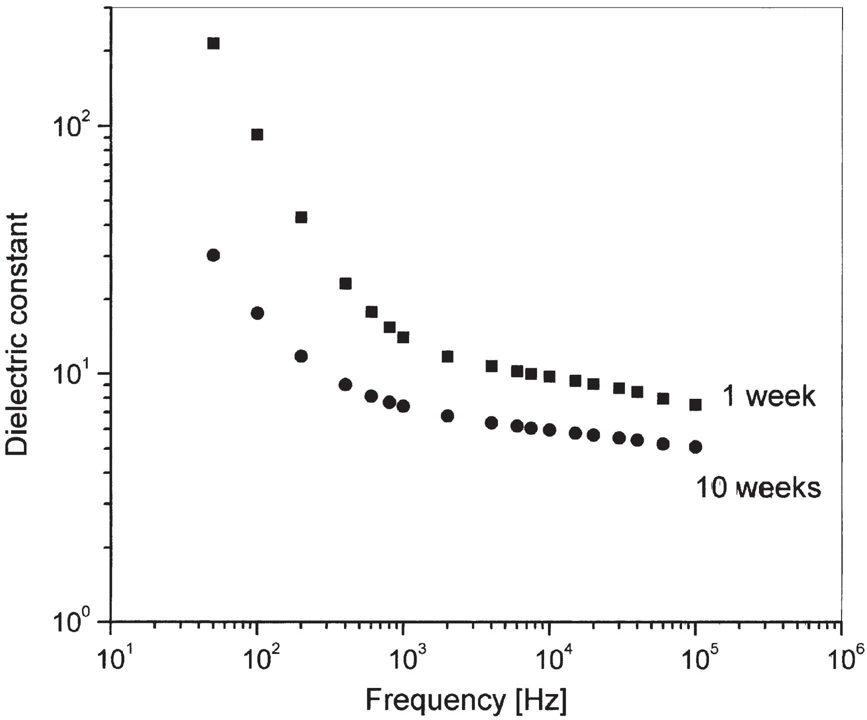

FIGURE 1 Spectrum of the dielectric constant for typical samples 5% of $CuSO_4$ by weight of PEO, at room temperature.

Figure 2 illustrates the behavior of the dielectric constant with temperature, for typical samples with 2% and 10% of $CuSO_4$ by weight of PEO, at a frequency of 1 kHz.

Figure 3 depicts the spectrum of the real part of conductivity, $\sigma'(\omega)$, obtained with the help of the relation $\sigma'(\omega) = \omega\varepsilon_0\varepsilon''(\omega)$, for typical samples of different contents of $CuSO_4$ at room temperature.

DISCUSSION OF RESULTS

Evidences of Ionic Transport

The increase of the dielectric constant with temperature shown in Figure 2, for typical samples with 2% and 10% of copper sulphate by weight of PEO, would be evidence that the observed dielectric response is mainly due to the migration of ions resulting from the dissociation of $CuSO_4$ inside the poly(ethylene oxide). This migration would be facilitated if an increase of the mean free volume was

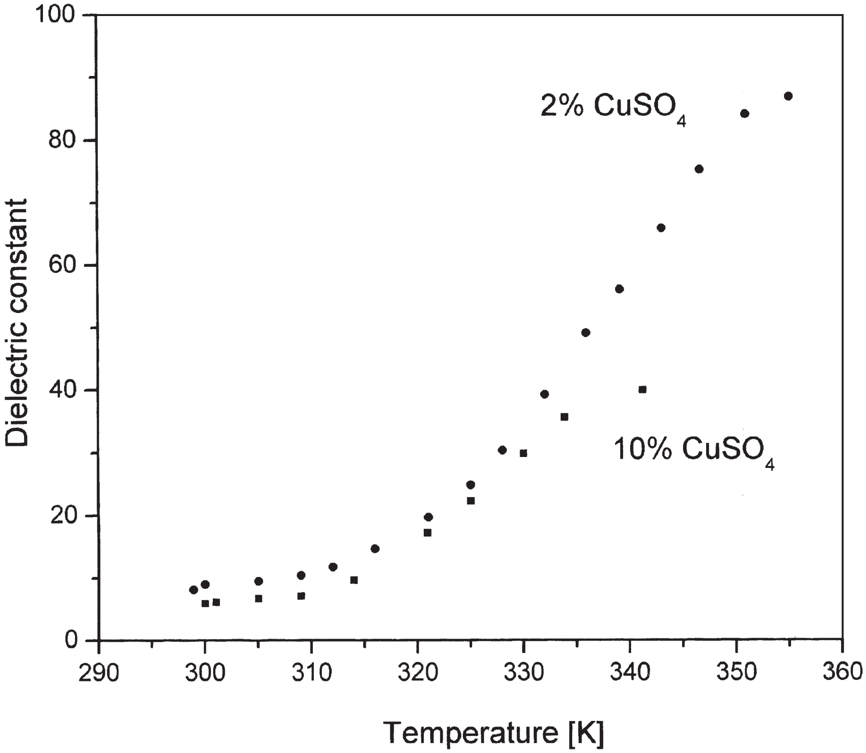

FIGURE 2 Behavior of the dielectric constant with temperature, for typical samples with two different contents of $CuSO_4$, at a frequency of 1 kHz.

assumed due to the thermal expansion of the medium. According to this argument, the increase of the dielectric constant ε' is a consequence of decreasing the Coulombian interaction among ions in the medium, so an increase of the ion conductivity is expected, by increasing the dielectric constant at a given frequency.

On the other hand, the arc diagram illustrated in Figure 4 does not show the semicircle expected for a Debye dielectric dispersion. The increase observed at the regions of low frequencies is an indication of the existence of a dc conductivity σ_0, this argument is compatible with the behavior of the real part of the observed electrical conductivity with frequency, depicted in Figure 3, which shows a tendency of the conductivity to reach a constant value at rather low frequencies, which one identifies as σ_0. Some methods for estimating the dc contribution from dielectric measurements has been reported elsewere [7–9]. In this report, the dielectric response was interpreted in the

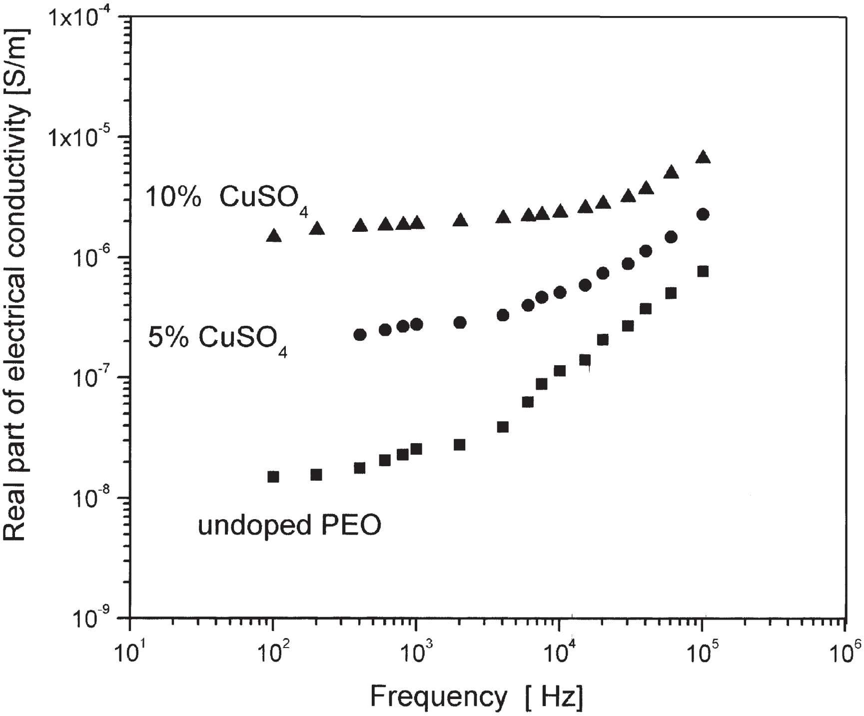

FIGURE 3 Spectrum of the real part of the electrical conductivity for typical samples with different contents of $CuSO_4$, at room temperature.

frame of the complex electrical modulus M* [10], defined as the inverse of the complex dielectric constant $\varepsilon^*(\omega)$. It is known that the complex dielectric constant for a particular material containing charge carriers with a dc conductivity σ_o, is given by [11],

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - I[\varepsilon''(\omega) + \sigma_o/\varepsilon_o\omega] \tag{1}$$

where ε_o is the permittivity of the free space.

The corresponding electrical complex modulus would be

$$M^* = [\varepsilon' + i(\varepsilon'' + \sigma_o/\varepsilon_o\omega)]/[\varepsilon'^2 + (\varepsilon'' - \sigma_o/\varepsilon_o\omega)^2] \tag{2}$$

when $\sigma_o/\varepsilon_o\omega \gg \varepsilon''(\omega)$, the imaginary part of Eq. 2 can be written as

$$M'' = (\sigma_o/\varepsilon_o\omega)/[\varepsilon'^2 + (\varepsilon'' - \sigma_o/\varepsilon_o\omega)^2] \tag{3}$$

a plot of Eq. 3 in a M″ vs. $\log\omega$ representation, would present a peak at a frequency given by

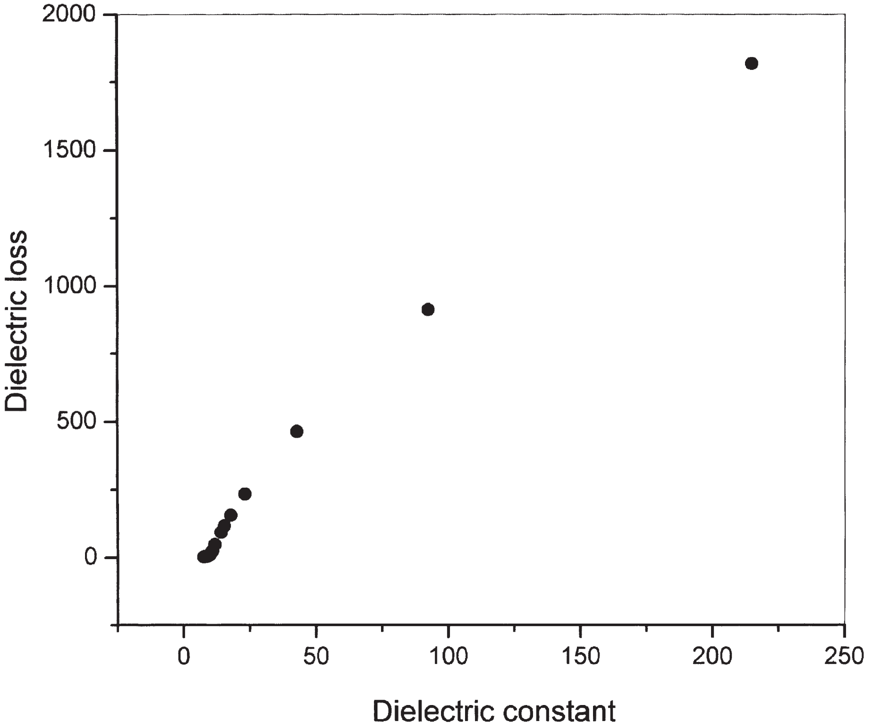

FIGURE 4 Arc diagram for a typical sample with a content of 5% of $CuSO_4$, at room temperature.

$$\omega_o = \sigma_o/\varepsilon_o\varepsilon_s \tag{4}$$

where ε_s is the low frequency limited dielectric constant. Figure 5 shows a plot M″ vs $\log\omega$ for typical samples at different contents of $CuSO_4$. Well-defined peaks are observed showing a displacement toward the regions of high frequencies by increasing the content of salt.

Behavior of the Ionic Conductivity with the Content of Salt

The fundamental equation for studying the electrical conductivity is given by:

$$\sigma = \sum_i n_i q_i \mu_i \tag{5}$$

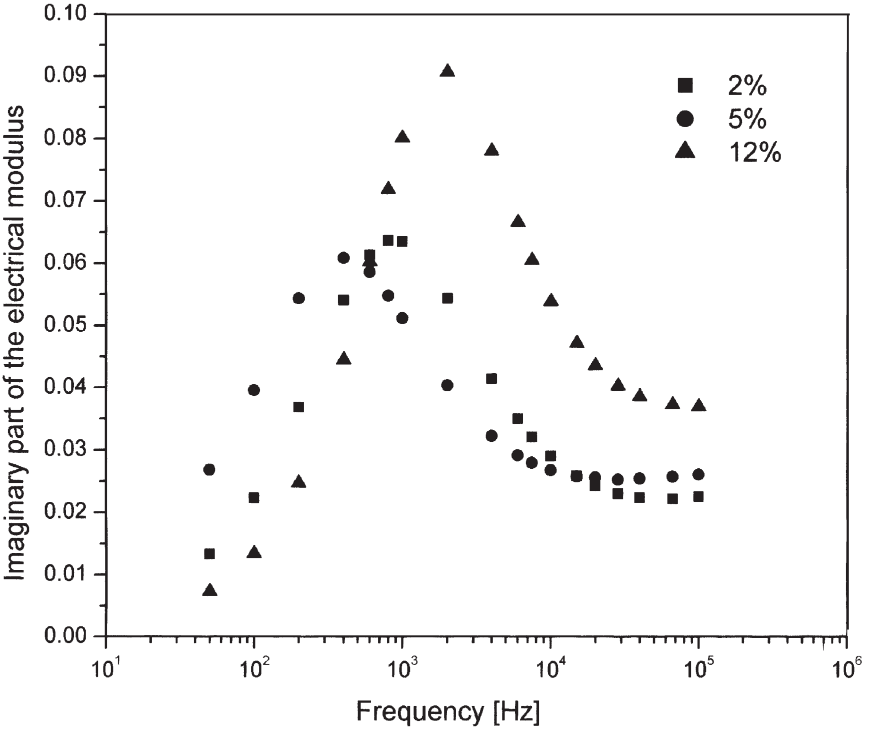

FIGURE 5 Spectrum of the imaginary part of the electrical modulus, for typical samples with different contents of $CuSO_4$, at room temperature.

where μ is the carriers mobility, n the number of carriers and q the correspondent electric charge. With the variation of salt concentration, although the charge remains constant, the ionic mobility and the number of charges change. Consequently, by increasing salt concentration, the conductivity increases because the number of charges and their mobility increase. Nevertheless, the rate of dissociation decreases by increasing the content of salt, such that at high concentration of salt the ionic mobility decreases. Therefore, the profile of the dc ionic conductivity in the range from low to high concentration of salt would show a maximum value at a given temperature. The displacement of the peaks toward high frequencies regions depicted in Figure 5 predicts, according to Eq. 4, an increase of dc conductivity with the salt concentration. Figure 6 shows the dc conductivity, obtained with the help of Eq. 4 and using the values of ω_0 from Figure 5, as a function of the content of $CuSO_4$. It is observed that the dc ionic conductivity increases by increasing the content of salt. However, the maximum

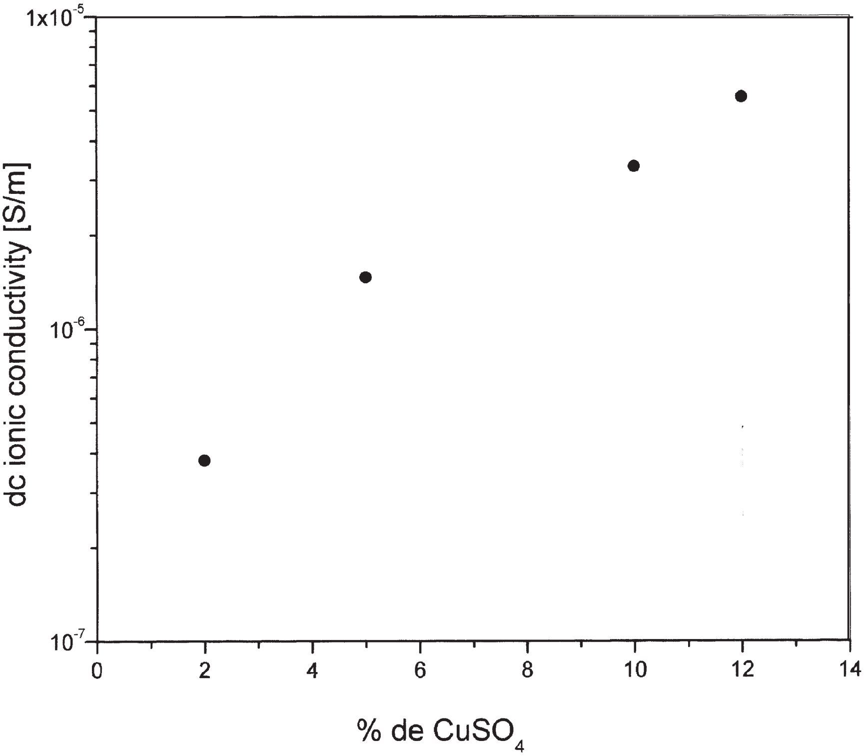

FIGURE 6 Behavior of the dc ionic conductivity with the contents of $CuSO_4$, at room temperature.

value expected at high concentration of salt was not possible to visualize in this study because samples with content of $CuSO_4$ above 12% by weight of PEO had very poor mechanical properties so they were not used for measurements. However, the profile in Figure 6 seems to show a tendency of the conductivity to reach such a maximum value at high concentration of salt.

Behavior of the Ionic Conductivity with Temperature

Figure 7 shows the variation with temperature of dc ionic conductivity for typical samples with 2% of $CuSO_4$, obtained from plots like illustrated in Figure 5, in a ln σ_0 vs 1/T representation. A bending of the curve can be observed that departs from a typical Arrhenius behavior, so it is not compatible with a simple thermal activation process. This kind of deviation has been commonly observed in polymer

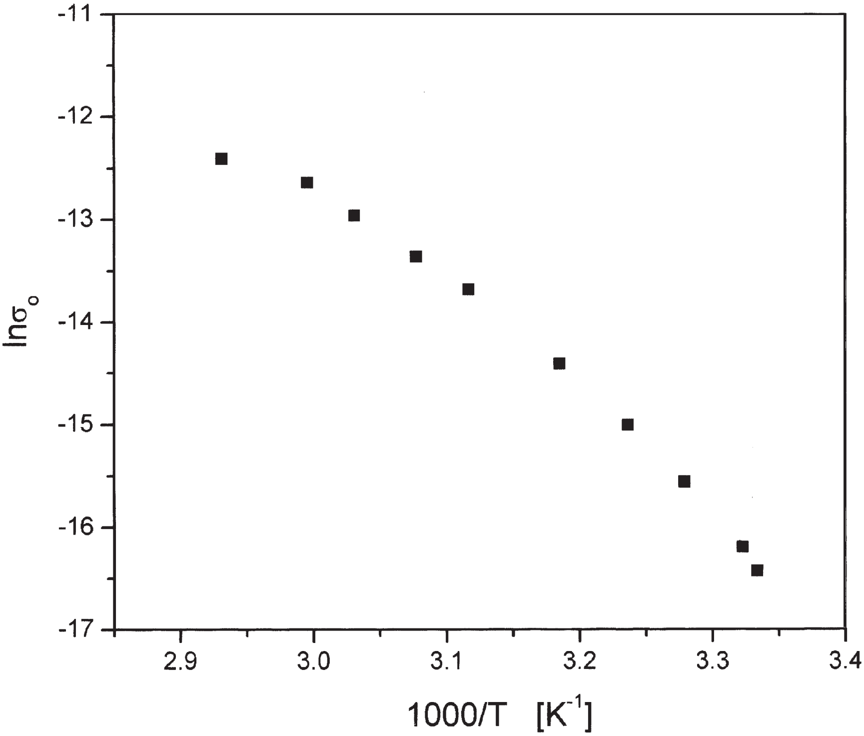

FIGURE 7 Temperature dependence of the dc ionic conductivity for typical sample with a content of 2% of $CuSO_4$ by weight of PEO, in an Arrhenius representation.

electrolytes and very often interpreted in terms of the free volume ideas [12–13]. Indeed, it was pointed out previously that the increase of the real part of the dielectric function (ε') by increasing temperature, shown in Figure 2, could be considered as an evidence of ionic transport and the ions' movement would be facilitated by the increase of the mean free volume (v_f) as a consequence of the material thermal expansion. The behavior of dc conductivity, observed in Figure 7, has been shown to fit an empirical formula of the form

$$T\sigma(T) = A\exp\{-\Delta E/k(T - T_o)\} \tag{6}$$

Eq. 6 is known as VTF behavior after the works of Vogel, Tamman, and Fulcher [14–16]. A and T_o are parameters that are calculated to give the best fit to the experimental points. ΔE can be considered as an apparent activation energy and would be visualized as the required energy for creating a suitable space for the migration of ions; the quantity $T - T_o$ would be a measure of the availability of this space.

In electrolyte polymers, very often T_o is estimated by using the relation $T_g - T_o \approx 50\,K$, where T_g is the glass transition temperature of the salt/polymer mixture [2]. In Figure 8, $\ln(T\sigma)$ is plotted against $1/(T - T_o)$ where T_g for this content of $CuSO_4$, obtained from DSC measurements, is in the order of 220 K. A straight line could be fitted, using linear regression, from whose slope and intercept with the $\ln(T\sigma_o)$-axis, the apparent activation energy ΔE and A parameters were estimated to be in the order of 0.20 eV and 1265.1 SK/m, respectively. Similar behavior was observed for all concentrations of copper sulphate with a moderate increase of the apparent activation energy with increasing content of salt.

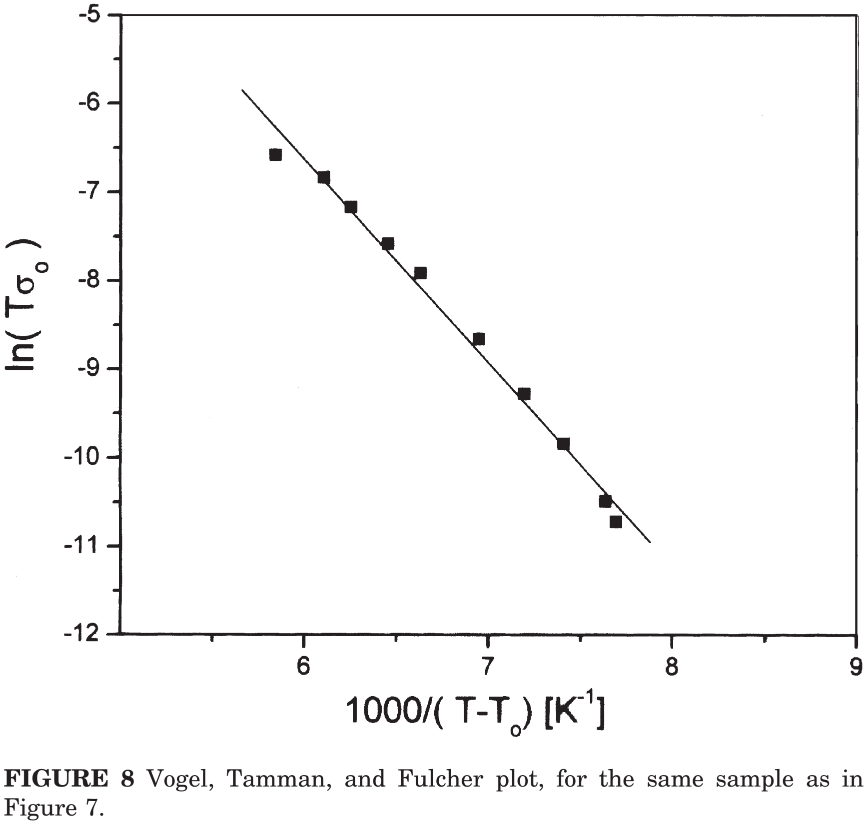

FIGURE 8 Vogel, Tamman, and Fulcher plot, for the same sample as in Figure 7.

CONCLUSIONS

An electrolyte polymer has been prepared using poly(ethylene oxide)/copper sulfate mixture (PEO/$CuSO_4$), with an ionic conductivity that increases with the content of $CuSO_4$, reaching a maximum value in the order of $5{,}5 \times 10^{-6}$ S/m, at room temperature for a content of 12% of $CuSO_4$ by weight of PEO. The behavior of conductivity with temperature is compatible with the free volume model through the empirical equation of Volmer, Tammann, and Fulcher. Although the free volume model presents some difficulties, it seem to be the simplest description to visualize, at least qualitatively, the diffusion of ions. It corresponds to the bending observed in the profile of the dc ionic conductivity with respect to temperature.

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