



Universidade de São Paulo

Biblioteca Digital da Produção Intelectual - BDPI

Departamento de Física e Ciência Interdisciplinar - IFSC/FCI

Artigos e Materiais de Revistas Científicas - IFSC/FCI

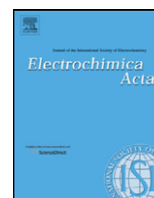
2011

Magnetic resonance and conductivity study of a gelatin-based polymer gel electrolyte

Electrochimica Acta, Amsterdam : Elsevier, v. 57, p. 187-191, 2011

<http://www.producao.usp.br/handle/BDPI/49805>

Downloaded from: Biblioteca Digital da Produção Intelectual - BDPI, Universidade de São Paulo



Magnetic resonance and conductivity study of a gelatin-based polymer gel electrolyte

A. Pawlicka^a, R.I. Mattos^a, J.F. Lima^b, C.E. Tambelli^c, C.J. Magon^b, J.P. Donoso^{b,*}

^a IQSC, Universidade de São Paulo, PO Box 780, 13560-970 São Carlos, SP, Brazil

^b IFSC, Universidade de São Paulo, PO Box 369, 13560-970 São Carlos, SP, Brazil

^c FZEA, Universidade de São Paulo, 13635-900 São Carlos, SP, Brazil

ARTICLE INFO

Article history:

Received 26 November 2010

Received in revised form 15 July 2011

Accepted 18 July 2011

Available online 23 July 2011

Keywords:

NMR

Conductivity

Proton conductor

EPR

Polymer gel electrolyte

Gelatin

ABSTRACT

This work reports results from proton nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR) and complex impedance spectroscopy of gelatin-based polymer gel electrolytes containing chloridric acid, cross-linked with formaldehyde and plasticized with glycerol. Ionic conductivity of 4×10^{-5} S/cm were obtained at room temperature for samples prepared with 0.1 M of HCl. Proton (¹H) lineshapes and spin-lattice relaxation times were measured as a function of temperature. Activation energies extracted from the ¹H NMR relaxation data are in the range of 23–25 kJ/mol. The EPR spectra, which were carried out in samples doped with copper perchlorate, were interpreted with the aid of an axial spin Hamiltonian and indicate the presence of two different Cu²⁺ species in axially distorted sites. Copper complexation with both hydrogen and nitrogen was verified by electron spin-echo envelope modulation (ESEEM) techniques.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Solid polymer electrolytes (SPE) have attracted considerable interest on account of their optical, mechanical and electrical properties [1–3]. Among various type of SPE, gel electrolytes obtained from plasticized polymers have drawn attention on account of their protonic conductivity [4–9]. Wiczorek et al. have reviewed the studies on nonaqueous conducting gel electrolytes. They discussed the effect of the solvent on the physical–chemical properties of the gel electrolyte and postulated Grothuss or vehicle-type proton transport mechanisms depending on the acid and the solvent used on the gel electrolyte [10].

The electrical properties and the magnetic resonance characterization of polymer electrolytes based on natural polymers, like starch, chitosan, agar and cellulose derivatives, were recently reviewed [11]. In recent years, a number of studies have addressed the electrical properties of proton-conducting polymer gel electrolytes formed by chitosan – phosphoric acid [12] and by chitosan – ammonium salts [13–17]. Recently we reported conductivity and magnetic resonance investigation on a gel electrolyte based on a gelatin network containing acetic acid (CH₃COOH) plasticized with glycerol and cross-linked with formaldehyde. Proton (¹H) nuclear

magnetic resonance (NMR) lineshapes and spin-lattice relaxation times measurements were used to characterize the proton mobility and electron paramagnetic resonance (EPR) experiments were carried out in samples doped with copper perchlorate in order to investigate the coordination environment of the cation in the gel electrolyte. The NMR results show that the proton mobility is dependent on acetic acid content in the gel electrolytes and the pulsed EPR electron spin echo envelope modulation (ESEEM) technique identified the involvement of both, hydrogen and nitrogen atoms, in the copper complexation of the gel electrolyte [18].

The present work focuses the gelatin-based polymer gel electrolytes containing chloridric acid, cross-linked with formaldehyde and plasticized with glycerol. NMR is an effective tool used in the study of ionic and polymer dynamics in polymer electrolytes [19–22]. As an element-selective method that is sensitive to local interactions, measurements of NMR line shapes, relaxation times and diffusion coefficients provide important information on the atomic motions that modulate these interactions.

2. Experimental

Electrolytes were prepared according to the following description. 2 g of commercial uncolored gelatin (Oetker®) was dispersed in 15 ml of HCl solutions with 0.1 M, 0.01 M and 0.001 M of chloridric acid, and heated under magnetic stirring up to 50 °C for complete dissolution. Glycerol as plasticizer and formaldehyde as

* Corresponding author.

E-mail address: donoso@ifsc.usp.br (J.P. Donoso).

Table 1
Sample compositions.

	Gelatin (wt%)	Glycerol (wt%)	Chloridric acid (M)	Formaldehyde (wt%)
Base	38	57	0	5
Sample 1	38	57	0.1	5
Sample 2	38	57	0.01	5
Sample 3	38	57	0.001	5

cross-linking agent were added to the solution under stirring. This viscous solution was then cooled down to room temperature and poured on Petri plates. The obtained transparent films were dried in a dry box for three days. Table 1 lists the composition of the samples investigated. The amorphous nature of the gel electrolytes was corroborated by powder X-ray diffraction and the transmittance of the film was analyzed by UV–vis spectroscopy. The samples were characterized by thermal analysis (DSC) and scanning electron microscopy (SEM). The ionic conductivities were obtained by measurements of the complex impedance in a Solartron model 1260 using an ac potential of 50 mV, for temperature and frequency ranging between 25–85 °C and 10 Hz–1 MHz, respectively. Proton (¹H) NMR linewidth and spin-lattice relaxation measurements were carried out from 170 K to 380 K using a home-built pulsed NMR spectrometer equipped with a TECPAG NMR kit, operating at 36 MHz, where a typical non-selective $\pi/2$ pulse length was of about 2 μ s. Nuclear spin-lattice relaxation times were determined using the standard saturation-recovery method, being the magnetization recoveries toward equilibrium found to be exponential throughout the entire temperature range. Continuous-wave (CW-EPR) and pulsed electron paramagnetic resonance spectra were obtained at 30 K and 16 K, respectively, on a Bruker Eleksys E580 spectrometer operating at 9.5 GHz. Temperature was controlled by a continuous flow liquid helium Oxford cryogenic system, model ITC503. For the electron spin-echo envelope modulation (ESEEM) experiments, the primary stimulated echo sequence (three-pulse) $\pi/2-T-\pi/2-\tau-\pi/2-\tau$ -echo was used. The microwave $\pi/2$ pulses were 8 ns long and the shot repetition time was 500 μ s. The ESEEM time domain traces were corrected for the exponential decay and a sine bell and a Hamming window function were applied, followed by zero filling and then Fourier transformed. The final spectrum is presented in the amplitude mode.

3. Results and discussion

3.1. Conductivity

Fig. 1 shows the Arrhenius plot of the ionic conductivity of the gel samples investigated. The ionic conductivity at 300 K of samples is 5.1×10^{-6} S/cm (base), 6.1×10^{-6} S/cm (sample 3), 8.7×10^{-6} S/cm (sample 2) and 4.3×10^{-5} S/cm (sample 1). It is possible to observe that the ionic conductivity increases monotonically with HCl concentration. It should be noted that these conductivity values are higher than those obtained before for the gelatin-based electrolyte prepared with acetic acid [18], but a quantitative comparison among these two systems is difficult to be established because of their different acid concentration: 18 wt% for the latter electrolyte compared to 0.1 M (i.e. 1 wt%) for the former one. Since strong acids may degrade the polymer gel electrolyte, the samples investigated were prepared with diluted HCl. However, the use of chloridric acid in these samples allowed increasing the glycerol concentration, which may explain the better ionic conductivity values observed. The increase in the conductivity with the temperature can be interpreted as a hopping mechanism between coordinating sites, hopping being assisted by local structural relaxations and segmental motions of the polymer salt complexes. From

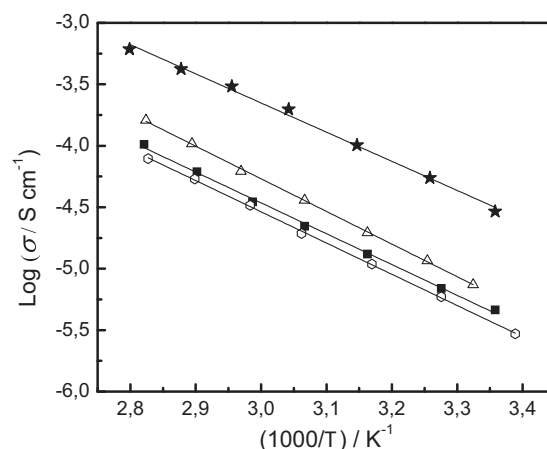


Fig. 1. Arrhenius plot of ionic conductivity of the gel electrolytes containing 0.1 M (★), 0.01 M (△) and 0.001 M (■) of chloridric acid, and the sample prepared without chloridric acid (○).

the fitting of the experimental data activation energies (E_a) values around 48 ± 3 kJ/mol (0.50 ± 0.03 eV) were obtained for the three samples.

3.2. Nuclear magnetic resonance

Fig. 2 shows the temperature dependence of the ¹H NMR linewidth (or, full-width-at-half-intensity) in the gel electrolyte samples studied here. The broad spectrum observed at low temperature shown in the insert of Fig. 2, consist of narrow peak flanked by a broader pair of lines that results from the dipole–dipole intra- and inter-molecular interactions between the protons of the different molecular groups, such as the CH₂ and NH₂ groups of the gelatin and the OH and CH₃ groups of the glycerol. Above 200 K, the mobility of the protons in the gel electrolyte increases enough to average out the H–H magnetic dipole–dipole interactions producing a line narrowing. Intra- and inter-molecular dipolar interactions between protons are reduced by local molecular motions, such as CH₂, CH₃ and NH₂ rotations and the proton diffusion at higher temperature. The abrupt decrease in line-width results in a residual line-width that is only a small fraction of the initial low-temperature rigid lattice value. Only one line narrowing onset was observed at 200 K. It

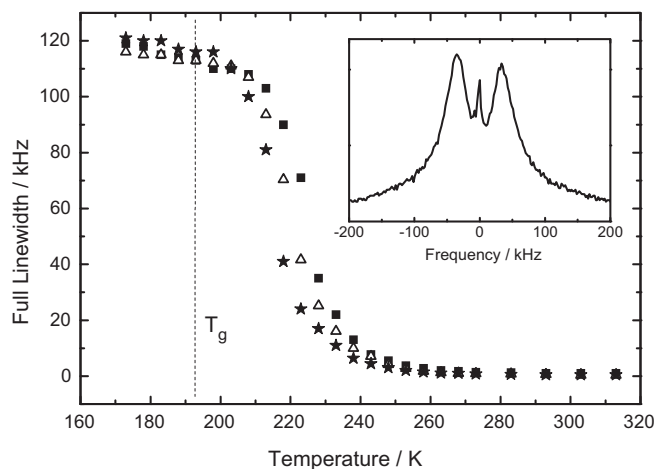


Fig. 2. Temperature dependence of the ¹H NMR linewidth in the gel electrolytes containing 0.1 M (○), 0.01 M (△) and 0.001 M (●) of chloridric acid, measured at the Larmor frequency of 36 MHz. The dashed line indicates the calorimetric glass transition temperature, 192 ± 5 K obtained from the DSC analysis of both samples. The insert shows the spectrum of sample 1 at 173 K.

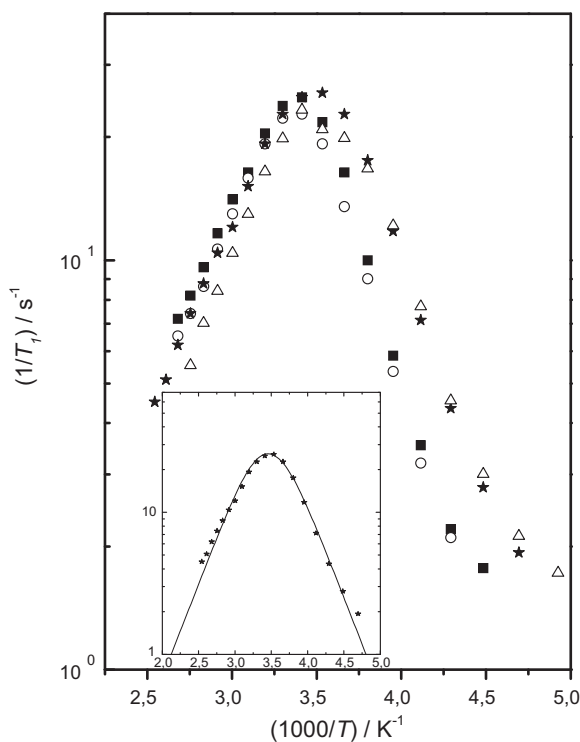


Fig. 3. Temperature dependence of the ^1H spin-lattice relaxation rates (T_1^{-1}) in the gel electrolytes measured at the Larmor frequency of 36 MHz. Sample 1 (\star), sample 2 (Δ), sample 3 (\blacksquare), and the sample prepared without chloridric acid (\circ). The solid line in the insert is the BPP fitting to the data of sample 1.

is clear from the data that the onset of motional narrowing occurs at about the calorimetric glass transition temperature ($T_g \approx 192 \pm 5$ K), a correspondence that is well established in polymer electrolytes [23,24]. The temperature range for the complete transition of the proton line is less than 40 K for both gel electrolytes. The activation energy for the line narrowing processes observed in Fig. 2, obtained by assuming a thermally activated process, following Arrhenius temperature dependence for the correlation time, yields 40 ± 4 kJ/mol (0.41 ± 0.04 eV) for the sample 1, 46 ± 4 kJ/mol (0.47 ± 0.04 eV) for the sample 2 and 50 ± 4 kJ/mol (0.52 ± 0.04 eV) for the sample 3.

The temperature dependence of the ^1H NMR spin-lattice relaxation rates (T_1^{-1}) of the gel electrolytes containing 0.1 M, 0.01 M and 0.001 M of HCl and also the sample prepared without chloridric acid are displayed in Fig. 3. The proton spin-lattice relaxation arises from the modulation of the proton–proton dipolar interactions caused by a series of dynamic processes, such as reorientational and vibrational motions of the CH_3 , CH_2 and NH_2 groups in the gelatin and the glycerol, and the mobility arising from proton diffusion.

Within the Bloembergen, Purcell and Pound (BPP) model, which assume non-correlated isotropic random motions, the relaxation rate T_1^{-1} can be expressed in terms of the spectral density function $J(\omega_0\tau)$ evaluated at the NMR Larmor frequencies ω_0 and $2\omega_0$ of the nuclei with spin I [18]:

$$\frac{1}{T_1} = C[J(\omega_0\tau) + 4J(2\omega_0\tau)]. \quad (1)$$

The spectral density function is parameterized by the Larmor frequency, ω_0 , and the correlation time, τ , of the proton motion modulating the spin interactions. An Arrhenius temperature dependence for the correlation time is often assumed, $\tau = \tau_0 \exp(E_a/k_B T)$, where k_B is the Boltzmann constant, E_a is the activation energy and τ_0 is the pre-exponential factor, which is of the order of an optical phonon frequency (10^{12} – 10^{14} s $^{-1}$). The constant

C in Eq. (1) depends on the particular spin interaction responsible for the relaxation. In the case of the ^1H resonance in polymer electrolytes the constant C is related to the mean-square amplitude of the fluctuating proton–proton dipole–dipole interactions. The spectral density function in the framework of the BPP model is

$$J(\omega) = \frac{\tau_c}{1 + \omega^2\tau_c^2} \quad (2)$$

Eqs. (1) and (2) predict the presence of a spin-lattice relaxation rate maximum at a given temperature, T_{max} , at which the condition $\omega_0\tau_c \approx 0.62$ is fulfilled. One can compare the relative mobility of the proton in different samples by comparing their T_{max} . We observed that when the sample is prepared only with gelatin and formaldehyde (without glycerol and acid) the spin lattice relaxation rate become almost temperature independent, about 10 s $^{-1}$ in the temperature range of 250–380 K, indicating the gelatin do not contribute for the relaxation processes. However, when the glycerol is introduced in the polymer, a symmetric spin-lattice relaxation rate maximum is observed in this same temperature range (base sample in Fig. 3). This indicates that the presence of glycerol is responsible for relaxation maximum observed. When HCl concentration is increased, the T_{max} shifts to lower temperatures. The shift in T_{max} for sample 1 toward lower temperature reflects the enhancement of the proton mobility when a larger amount of HCl is introduced in the gel electrolyte. This behavior is consistent with the ^1H motional narrowing data, where the transition temperature of sample 1 occurs below those of the sample 2, sample 3 and sample without HCl (Fig. 2) and is consistent with the higher conductivity obtained for this electrolyte (Fig. 1). Table 2 summarizes the parameters (T_{max} , E_a and τ_0) obtained from the fitting of the ^1H NMR relaxation data with Eqs. (1) and (2). The BPP fitting of sample 1 data can be verified in the insert of Fig. 3.

The most interesting feature of the data in Fig. 3 is the symmetrical inverted-V-shape of the relaxation curves for the three gels investigated. This behavior is in contrast with those observed in the gel electrolytes prepared with acetic acid, which displayed an asymmetric shape around the relaxation rate maximum. These asymmetric curves were interpreted by assuming the existence of two distinct proton dynamics, one associated with the protons of the acetic acid and another one caused by protons in different environments [18]. Possibly, the asymmetry of the relaxation curves in Fig. 3 is not discernible because the samples were prepared with a more diluted acid. As mentioned above, the acid content in the electrolyte gels prepared with acetic acid (18–33 wt%) is higher than the electrolyte prepared with chloridric acid (less than 1 wt%).

3.3. Electron paramagnetic resonance

In order to investigate the coordination environment of the cation in the gel electrolyte we undertake an EPR investigation on samples slightly doped with copper perchlorate. EPR is a well-known sensitive experimental technique for the characterization of local order in non-crystalline systems. It has proven to be extremely useful to investigate the location, nature and coordination environment of small concentration of paramagnetic centers, such as transition metals ions or rare earth ions [25–28].

Fig. 4 shows the X-band CW-EPR spectrum measured at 30 K of sample 1 doped with 0.001 M copper perchlorate. The spectrum shows the presence of the paramagnetic Cu^{2+} ions in axially distorted sites. CW-EPR spectrum of the gel electrolyte consists of a set of four hyperfine lines in the low field part of the spectra, which are due to the dipole–dipole interaction between the magnetic moment of the ^{63}Cu and ^{65}Cu nucleus and the electronic moment of the unpaired Cu^{2+} electron. The Cu^{2+} ion has a $3d^9$ electronic configuration and spin $S = 1/2$. The nuclear spin for both ^{63}Cu (natural abundance 69%) and ^{65}Cu (natural abundance 31%) isotopes

Table 2
NMR parameters obtained from ^1H NMR line narrowing and spin lattice relaxation rates in the polymer gel electrolytes with different chloridric acid concentrations. E_a is the activation energy for the motion causing the proton relaxation and τ_0 is the pre-exponential factor of the Arrhenius temperature dependence of the correlation time.

	Base	Sample 1	Sample 2	Sample 3
T_{max} (K)	301	287	289	295
E_a	28.0 kJ/mol(0.29 eV)	25.1 kJ/mol(0.26 eV)	24.1 kJ/mol(0.25 eV)	23.2 kJ/mol(0.24 eV)
τ_0 ($\times 10^{-13}$ s)	0.04	0.80	1.10	2.10

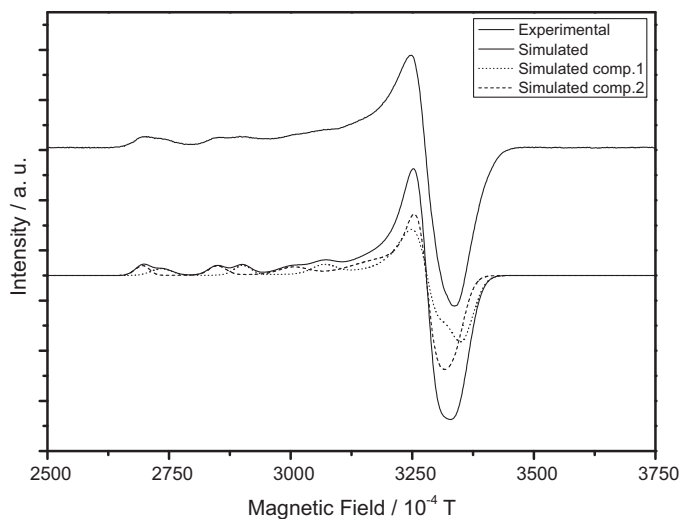


Fig. 4. X-band CW-EPR spectrum measured at 30 K of the gel electrolyte (sample 1) doped with 0.001 M of copper perchlorate.

is $I=3/2$, both with closely similar nuclear moments. Therefore $(2I+1)$, i.e. four perpendicular and four parallel hyperfine components could be expected. In the high field part (or, perpendicular part) of the spectra in Fig. 4, the copper hyperfine satellites are not resolved and a single line with a small structure is observed. A closer examination of the line shape in the parallel region reveal that the experimental spectrum is a superposition of two spectral components, corresponding to two different copper species. Taking into account the hyperfine interaction, each component of the EPR spectrum can be interpreted by means of an axial spin Hamiltonian,

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\parallel}I_z S_z + A_{\perp}(I_x S_x + I_y S_y) \quad (3)$$

where β is the Bohr magneton, H_i are the component of the magnetic field; S and I are the electron and the nuclear spin operators; g_{\parallel} and g_{\perp} are the parallel and perpendicular components of the anisotropic g tensor, and A_{\parallel} and A_{\perp} are the parallel and perpendicular hyperfine components of the hyperfine tensor A . The experimental Cu^{2+} EPR spectrum was analyzed by numerical simulation of the spin Hamiltonian (Eq. (3)) for both copper species (dotted lines in Fig. 4). The best fitting of the experimental spectra were achieved for the Hamiltonian spin parameters given in Table 3. It should be noted that no apparent difference is observed between the EPR spectra in Fig. 4 and those previously observed for the gelatin-based electrolyte prepared with acetic acid [18], except for the hyperfine lines which are broader for the former electrolyte. The empirical model of Blumberg and Peisach, which correlates the pair $(g_{\parallel}, A_{\parallel})$ of Cu^{2+} EPR parameters to the bonding nature of the

Table 3
Summary of the spin Hamiltonian parameters of Cu^{2+} doped gel electrolyte (sample 1) obtained from the simulation of the experimental EPR spectrum measured at 30 K.

	Area	g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}
Component 1	42%	2.270 (2)	2.062 (3)	18.4 mT	0.60 mT
Component 2	58%	2.315 (2)	2.062 (3)	17.3 mT	0.35 mT

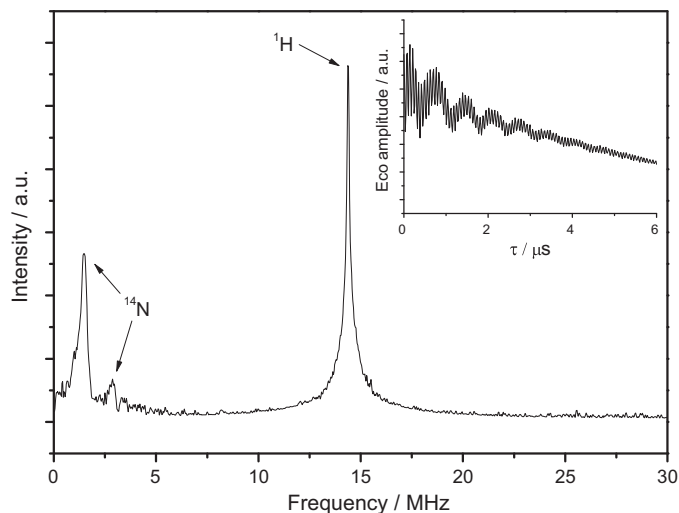


Fig. 5. X-band electron spin-echo envelope modulation (ESEEM) spectrum of sample 1 doped with 0.001 M of copper perchlorate, at magnetic field of 330 mT and microwave frequency of 9.7621 GHz. The echo amplitude decay is shown in the inset and the Fourier transform (at the bottom) denotes the peaks corresponding to the interaction of the Cu^{2+} unpaired electron with hydrogen and nitrogen nuclei neighbors.

Cu^{2+} in copper complexes [29], suggests that in the gel electrolyte the copper is coordinated to one nitrogen and three oxygen.

The coordination of hydrogen and nitrogen atoms to the copper in the gel electrolyte is verified by using the pulsed EPR technique named ESEEM (electron spin echo envelope modulation). Fig. 5 shows the X-band ESEEM results of sample 1, measured at 16 K and at the field position corresponding to the maximum in the absorption spectrum, which corresponds to the center of the perpendicular portion of the derivative CW spectrum of Fig. 4. In the echo amplitude decay (insert) one can notice the presence of both, a fast and a less intense slow modulation, attributed to the interaction of the Cu^{2+} unpaired electron with hydrogen and nitrogen neighboring nuclei, respectively. Only one peak is observed at the hydrogen nuclear frequency, what is an indication of weak electron–hydrogen hyperfine coupling. In the case of an electron spin $S=1/2$ coupled to a single ^{14}N ($I=1$) the ESEEM spectrum can be more complex, leading to a structure that can be composed by none, one, two or three narrow lines [30]. The observation of two lines in Fig. 5, at the nitrogen hyperfine frequencies, is an indication of strong electron–nitrogen couplings. This result is very similar to what has been observed before [18] and indicates that both, the ^1H nuclei (of the gelatin and the plasticizer) and the ^{14}N nuclei (of the glycine and proline groups of the gelatin) are close enough to interact with the copper ion. These two different environments for the copper can explain the observation of two different copper species in the CW-EPR spectrum.

4. Conclusions

Gelatin-based electrolytes with protonic conduction are promising macromolecules to be applied as ionic conducting membranes for electrochromic devices [31] and in this paper we report

conductivity, ^1H NMR lineshapes and relaxation times and EPR measurements in polymer gel electrolytes formed by gelatin plasticized with glycerol, cross-linked with formaldehyde and containing chloridric acid. Conductivity of 4×10^{-5} S/cm was obtained at room temperature for samples prepared with 0.1 M of chloridric acid. All samples are amorphous and show good thermal and chemical stability. The temperature dependence of the ^1H spin-lattice relaxation shown a well-defined rate maximum whose position depend on the acid concentration of the gel electrolyte, reflecting the high proton mobility in these membranes. The EPR spectrum of the sample doped with copper perchlorate indicates the presence of the paramagnetic Cu^{2+} ions in axially distorted sites. The line-shape in the parallel region reveal the presence to two different copper species. The good ionic conductivity values of the transparent, self-sustaining and flexible membranes based on gelatin and containing chloridric acid confirm its promising application as gel electrolytes in electrochemical devices.

Acknowledgments

The financial support of the Brazilian Agencies Capes, CNPq and FAPESP are gratefully acknowledged.

References

- [1] M. Armand, *Solid State Ionics* 69 (1994) 309.
- [2] P.G. Bruce (Ed.), *Solid State Electrochemistry*, Cambridge University Press, 1995, p. 111.
- [3] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359.
- [4] W. Wieczorek, G. Zukowska, D. Ostrovskii, Z. Florjanczyk, *J. Phys. Chem. B* 105 (2001) 9686.
- [5] K.R. Jeffrey, W. Wieczorek, D. Raducha, J.R. Stevens, *J. Chem. Phys.* 110 (1999) 7474.
- [6] K.R. Jeffrey, G.Z. Zukowska, J.R. Stevens, *J. Chem. Phys.* 119 (2003) 2422.
- [7] A. Awadhia, S.L. Agrawal, *Solid State Ionics* 178 (2007) 951.
- [8] H.P.S. Missan, S.S. Sekhon, *Ionics* 15 (2009) 635.
- [9] H. Gao, Q. Tian, K. Lian, *Solid State Ionics* 181 (2010) 874.
- [10] W. Wieczorek, G. Zukowska, R. Borkowska, S.H. Chung, S. Greenbaum, *Electrochim. Acta* 46 (2001) 1427.
- [11] C.A.C. Sequeira, D.M.F. Santos (Eds.), *Polymers Electrolytes: Fundamentals and Applications*, Woodhead Publishing, 2010.
- [12] S.R. Majid, A.K. Arof, *Physica B* 390 (2007) 209.
- [13] L.S. Ng, A.A. Mohamad, *J. Membr. Sci.* 325 (2008) 653.
- [14] A. Jamaludin, A.A. Mohamad, *J. Appl. Polym. Sci.* 118 (2010) 1240.
- [15] J.F. Du, Y. Bai, D.A. Pan, W.Y. Chu, L.J. Qiao, *J. Polym. Sci. B* 47 (2009) 549.
- [16] M.F.Z.A. Kadir, L.P. Teo, S.R. Majid, A.K. Arof, *Mater. Res. Innov.* 13 (2009) 259.
- [17] M.F.Z. Kadir, S.R. Majid, A.K. Arof, *Electrochim. Acta* 55 (2010) 1475.
- [18] R.I. Mattos, A. Pawlicka, J.F. Lima, C.E. Tambelli, C.J. Magon, J.P. Donoso, *Electrochim. Acta* 55 (2010) 1396.
- [19] M. Forsyth, M. Garcia, D.R. MacFarlane, P. Meakin, S. Ng, M.E. Smith, *Solid State Ionics* 85 (1996) 209.
- [20] S.H. Chung, P. Heitjans, R. Winter, W. Bzaucha, Z. Florjanczyk, Y. Onoda, *Solid State Ionics* 112 (1998) 153.
- [21] R. Böhmer, K.R. Jeffrey, M. Vogel, *Progr. NMR Spectrosc.* 50 (2007) 87.
- [22] H. Walderhaug, O. Söderman, D. Topgaard, *Progr. NMR Spectrosc.* 56 (2010) 406.
- [23] S.H. Chung, K.R. Jeffrey, J.R. Stevens, *J. Chem. Phys.* 94 (1991) 1803.
- [24] A.M. Regiani, C.E. Tambelli, A. Pawlicka, A.A.S. Curvelo, A. Gandini, J.-F. LeNest, J.P. Donoso, *Polym. Int.* 49 (2000) 960.
- [25] J.R. Pilbrow, *Transition Ion Electron Paramagnetic Resonance*, Oxford University Press, 1990.
- [26] P.J. Carl, S.C. Larsen, *J. Phys. Chem. B* 104 (2000) 6568.
- [27] K. Kruczala, S. Schlick, *J. Phys. Chem. B* 103 (1999) 1934.
- [28] J.P. Donoso, M.G. Cavalcante, T.J. Bonagamba, O.R. Nascimento, H. Panepucci, *Electrochim. Acta* 40 (1995) 2357.
- [29] J. Peisach, W.E. Blumberg, *Arch. Biochem. Biophys.* 165 (1974) 691.
- [30] Y. Deligiannakis, M. Louloud, N. Hadjiliadis, *Coord. Chem. Rev.* 204 (2000) 1.
- [31] A. Al-Kahlout, D. Vieira, C.O. Avellaneda, E.R. Leite, M.A. Aegerter, A. Pawlicka, *Ionics* 16 (2010) 13.