

Ionic Conductivity–Structure Property Relationship in Gel Electrolytes on the Basis of Oligo(ethylene glycol)₂₃ Dimethacrylate Plasticized with Oligo(ethylene glycol)₁₁ Dimethyl Ether

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This paper reports dielectric spectroscopic studies completed by electrochemical measurements in combination with DSC and PFG-NMR investigations to study the charge carrier transport in gel electrolytes, which were prepared by photoinitiated polymerization of oligo(ethylene glycol)₂₃ dimethacrylate [(EG)₂₃DMA] in the presence of oligo(ethylene glycol)₁₁dimethyl ether [(EG)₁₁DME] as plasticizer and LiCF₃SO₃. The resulting films show a glass transition at about $-60\text{ }^{\circ}\text{C}$ and the melting of the plasticizer around $-12\text{ }^{\circ}\text{C}$. Below the glass transition two relaxation processes were observed by dielectric spectroscopy, which most likely are to be related to the γ relaxation of the EG groups and the β relaxation of the methacrylate groups. The high-temperature behavior of the dielectric response is dominated by the conductivity, which is weakly dependent on the frequency in this temperature range. The permittivity goes through a maximum at room temperature and decreases with further enhancement of the temperature in connection with an increase in ionic aggregation indicated by growing deviations from the Nernst–Einstein relationship. These deviations expressed as a Haven ratio are discussed as the contribution of bounded species that do not take part in the conductivity to the overall diffusivity, either by an enlarged content of these species, c_b , or by an enhancement of their self-diffusivity, D_b .

Introduction

Gel electrolytes are hopeful candidates for electrolyte materials in lithium batteries. For further improvement of their properties, a better understanding of the role of the plasticizer and the polymer concerning the ionic transport is necessary.

We have focused our studies on gel electrolytes on the basis of homopolymers and copolymers of oligo(ethylene glycol) dimethacrylates plasticized with various oligo(ethylene glycol) derivatives.^{1–5} A significant amount of research work has been published in the literature on the properties of polymer electrolytes on the basis of comb branched poly(methyl methacrylate)s with oligo(ethylene glycol) units in the side chains⁶ or poly(methyl methacrylate)s grafted with PEO⁷ and on gels based on PMMA.^{8,9} Contrary to most of these systems, our intention was to prepare mechanically stable electrolyte films by chemically cross-linking in one step in the presence of plasticizer and salt.

In these gel electrolyte systems the charge carrier diffusivity and hence the conductivity of the gel electrolyte systems are strongly related to the plasticizer diffusivity as recent investigations of the ionic conductivity in combination with the measurement of the self-diffusion coefficients of plasticizer and charge carriers (PFG-NMR) have shown.^{3,5}

The polymer guarantees the mechanical strength of the gel electrolytes. Furthermore, the oligo(ethylene glycol) (EG) segments of the polymer coordinate cations in competition with the plasticizer. In consequence, the cationic transference

numbers of these gel electrolytes depend on the relation between the ability of the plasticizer and the polymer to coordinate cations.^{3,5} Generally, only one self-diffusion coefficient of the cations was observed by means of pulsed-field-gradient (PFG)-NMR.^{3,5,10,11} However, Forsyth^{12,13} or Clerizucio^{10,11} et al. could detect two relaxation processes for the lithium ions by ⁷Li T_2 and $T_{1\rho}$ relaxation time measurements in plasticized polyether based polymer electrolyte systems. The cations coordinated to the polymer move more slowly and hence relax faster than cations coordinated to the plasticizer.

It should be expected that the ionic transport is influenced by the degree of cross-linking. Indeed, ¹H spin–lattice relaxation time measurements of nonplasticized films of oligo(ethylene glycol)_{*n*} dimethacrylates ($n = 9, 14, 23$) show a shift of the T_1 minimum to higher temperatures if the chain length of the oligo(ethylene glycol) segments decreases indicating a decreasing flexibility of the network. However, in the presence of (EG)₁₁DME as plasticizer both the T_1 minimum and the conductivity are only slightly affected by the chain length of the oligo(ethylene glycol) segments, and consequently the conductivity should be governed by the mobility of the plasticizer^{14,15} in the case of these systems.

This paper reports dielectric spectroscopic studies completed by electrochemical measurements in combination with DSC and PFG-NMR investigations of gel electrolytes prepared by photoinitiated polymerization of oligo(ethylene glycol)₂₃ dimethacrylate [(EG)₂₃DMA] in the presence of oligo(ethylene glycol)₁₁ dimethyl ether [(EG)₁₁DME] as plasticizer and LiCF₃SO₃.

Dielectric Spectroscopy. Impedance and dielectric spectroscopy have the same experimental basis but were used with

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different intentions. The aim of the impedance spectroscopy is to study the conductivity and the electrochemical behavior of electrodes and electrolytes. Dielectric spectroscopy probes the dynamic and relaxation behavior of electric dipoles. The result, the complex dielectric function $\epsilon^*(\omega)$, consists of the dielectric permittivity ϵ' , which reflects the ability of the material to screen charge carriers or to dissolve salts, and the dielectric loss ϵ'' . The latter is related to the conductivity and to relaxation phenomena as described by the following equation:

$$\epsilon''(\omega) = \frac{\sigma_0}{\epsilon_0} \frac{1}{\omega^s} + \sum \epsilon''_{\text{Relax}_n} \quad (1)$$

The complex conductivity $\sigma^*(\omega)$ and the complex dielectric function $\epsilon^*(\omega)$ are related to each other by the following equation:

$$\sigma^*(\omega) = i\epsilon_0\omega\epsilon^*(\omega) \quad (2)$$

where ϵ_0 is the permittivity of free space and $\omega = 2\pi f$.

The dc conductivity σ_0 and the parameters of the relaxation processes as the dielectric strength $\Delta\epsilon_k$ ($\Delta\epsilon_k = \epsilon_{Si} - \epsilon_{\infty i}$) and the dielectric relaxation time τ can be calculated from the dielectric loss by means of the Havriliak–Negami function:^{16,17}

$$\epsilon''(\omega) = \frac{\sigma_0}{\epsilon_0} \frac{1}{\omega^s} + \sum \text{Im} \left[\frac{\Delta\epsilon_k}{(1 + (i\omega\tau_k)^{\alpha_k})^{\beta_k}} \right] \quad (3)$$

α_k and β_k are constants describing the magnitude and asymmetry of the relaxation, and s is an additional fitting parameter $0.5 < s < 1$, which quantifies the “non-ohmic behavior” due to electrode polarization effects.^{16,17}

For samples with a relatively high conductivity, the relaxation processes can be masked by the conductivity. This behavior is described for salt-containing PEO systems where only the γ and β processes are dielectrically active, and the α process (normally related to the glass transition) is not detectable in dielectric studies.^{18,19} Such a behavior should also be expected in our investigations.

The dielectric relaxation behavior of the investigated gel electrolytes should be dominated by the signals of the oligo-(ethylene glycol) (EG) units due to the high EG content of approximately 80 wt %. The relaxation of the methacrylate groups should take place at higher temperatures than for PEO²⁰ and should be masked therefore by conductivity too. Besides this, Maxwell–Wagner polarization is expected, which is often described in context with plasticized polymer systems.²¹

Self-Diffusion Coefficients. The conductivity contains contributions from all ionic species present in the sample. Each ionic species has its own mobility μ_i defined as the ratio between the drift velocity v_i and the electric field E acting on the ionic species:

$$\mu_i = v_i/E \quad (4)$$

Another dynamic quantity of the species is their self-diffusion coefficient D .

The self-diffusion coefficient is connected with the friction factor of the species f_i by the Stokes–Einstein equation

$$D_i = kT/f_i \quad (5)$$

where kT has its usual meaning.

f_i is defined by the force F that is necessary to move the species with the (constant) velocity v_i through a viscous medium.

F is equal to $z_i e E$ for a species with a charge $z_i e$ (where e is the elementary charge and z_i an integer), and f_i turns out to be

$$f_i = z_i e E / v_i = z_i e / \mu_i \quad (6)$$

We use Ohm’s law in the form

$$j = \sigma E \quad (7)$$

which is equal to

$$j = e N_A (z_+ c_+ v_+ + z_- c_- v_-) \quad (8)$$

for anionic and cationic species, using the flow equation $j = \rho v$. ρ denotes the number density of charge carriers, c the molar concentration of charged species, and N_A the Avogadro constant.

We arrive after a few steps at the well-known Nernst–Einstein equation, which connects the conductivity σ with the self-diffusion coefficients D_+ and D_- of the cations and anions:

$$\sigma = (e^2 N_A / kT) (z_+ c_+ D_+ + z_- c_- D_-) \quad (9)$$

The measurement of the self-diffusivity of the anions and cations allows the determination of their individual contribution to the charge transport (conductivity) and consequently of the transference numbers $t^+ = D_+ / (D_+ + D_-)$ and $t^- = D_- / (D_+ + D_-)$.

The pulsed-field-gradient NMR is a very convenient and well-established method to measure the self-diffusivity of molecular species with NMR-active nuclei, which was already used to study the charge carrier mobility in polymer electrolyte systems.^{10,11,22,23} In the gel electrolytes studied in this work, the self-diffusivity of three mobile species can be measured separately by PFG-NMR, the cation self-diffusion by ⁷Li NMR, the anion self-diffusion by ¹⁹F NMR, and the plasticizer self-diffusion by ¹H NMR.^{3,5}

Concerning the ionic diffusion, one has to have in mind however that PFG-NMR measures the motion of the ensembles of lithium and fluorine nuclei in different states. Polymer electrolytes are extremely nonideal due to the low dielectric constant; hence, the degree of ionic association is relatively high. Anions can be free or can be a part of ion pairs, of higher charged or even uncharged ionic aggregates. Lithium ions should be bounded in every case because of the extraordinarily high charge radius relation and can be coordinated to the plasticizer or to the polymer or even be part of charged and uncharged ionic associates. This explains the lower mobility of the lithium ions relative to the mobility of the plasticizer and the anions, as usually observed,^{3,5,10,11,22} and the fact that the self-diffusion coefficients of the charge carriers and the plasticizer in magnitude and in their activation energies are close together.^{3,5,23} To reach a high cation mobility, cations should essentially be attached to the plasticizer and not to the polymer.⁵

Furthermore, we have to assume a fast exchange of the species between these different ionic states discussed above within the time scale of the PFG-NMR experiment, which is typically between 10 and 100 ms. Hence, the measured self-diffusion coefficients $D_{\text{exp}}(\text{Li})$ and $D_{\text{exp}}(\text{F})$ are averaged values with contributions from lithium nuclei and fluorine nuclei in ionic species of a free solvated state, $D_f(\text{Li}) \equiv D_+$ and $D_f(\text{F}) \equiv D_-$, and of a bound state, $D_b(\text{Li})$ and $D_b(\text{F})$, i.e., species which contribute to the conductivity and which do not.

$$D_{\text{exp}}(\text{Li}) = (c_f/c_{\text{tot}})D_f(\text{Li}) + (c_b/c_{\text{tot}})D_b(\text{Li}) \quad (10)$$

$$D_{\text{exp}}(\text{F}) = (c_f/c_{\text{tot}})D_f(\text{F}) + (c_b/c_{\text{tot}})D_b(\text{F}) \quad (11)$$

with $c_f + c_b = c_{\text{tot}}$. In a first approximation the same c_f was used for lithium and fluorine species.

The assumption of the case of fast exchange is verified in the experiment by the fact that always only one diffusivity of lithium and fluorine nuclei is observed (see below). The eqs 10 and 11 can be rationalized as the consequence of a hopping process of the ions between the free and the bound state. A fraction c_f/c_{tot} of the time is effective for diffusion in the free state, while the fraction c_b/c_{tot} of the time is effective for diffusion in the bound state.

In the Nernst–Einstein eq 9, only $c_f D_f(\text{Li})$ and $c_f D_f(\text{F})$ have to be inserted, and we obtain for σ with eqs 10 and 11

$$\sigma = (e^2 N_A / kT) \{ c_{\text{tot}} (D_{\text{exp}}(\text{Li}) + D_{\text{exp}}(\text{F})) - c_b (D_b(\text{Li}) + D_b(\text{F})) \} \quad (12)$$

Assuming a slow self-diffusion of the bound species and/or a low concentration c_b , i.e.

$$c_b (D_b(\text{Li}) + D_b(\text{F})) \ll c_f (D_f(\text{Li}) + D_f(\text{F})) \quad (13)$$

we can neglect the second term in eqs 10, 11, and 12 and obtain

$$\sigma = (e^2 N_A / kT) c_{\text{tot}} (D_{\text{exp}}(\text{Li}) + D_{\text{exp}}(\text{F})) \quad (14)$$

The Nernst–Einstein equation is often used in this or in a similar form in the literature of PFG-NMR studies on polymer electrolytes.^{10,11,22}

If we cannot neglect the second term in eq 12, deviations from the Nernst–Einstein equation will be observed; that is, the conductivity calculated with eq 14 will differ from the measured dc conductivity. This is the normal behavior in the field of polymer electrolytes.^{22–24} These deviations are often expressed by the Haven ratio $H_R = D_{\text{exp}}/D_\sigma$ (here D_{exp} is the sum of $D_{\text{exp}}(\text{Li})$ and $D_{\text{exp}}(\text{F})$ and D_σ is a self-diffusivity calculated with $D_\sigma = kT\sigma/e^2 N_A c_{\text{tot}}$) and are explained as an expression of the correlated motion of the charge carriers.^{22–24} Following the discussion above, the Haven ratio should be better written using the full expressions of $D_{\text{exp}}(\text{Li})$ and $D_{\text{exp}}(\text{F})$ of eq 12:

$$H_R = \{ D_{\text{exp}}(\text{Li}) + D_{\text{exp}}(\text{F}) \} / \{ D_{\text{exp}}(\text{Li}) + D_{\text{exp}}(\text{F}) - (c_b/c_{\text{tot}})(D_b(\text{Li}) + D_b(\text{F})) \} \quad (15)$$

Hence, deviations from the Nernst–Einstein equation arise from the contribution of the diffusivity of bound species (which do not take part in the conductivity) to the self-diffusion coefficient D_{exp} , determined by the PFG-NMR experiment, and can be explained by (i) a high content of the bound species c_b and/or (ii) a high diffusivity of the bound species D_b . Only with validity of eq 13 will the Haven ratio be equal to 1.

Experimental Section

Materials and Film Preparation. Information concerning the purification and the drying process of the salt, the plasticizer, and the monomer and the preparation of the gel electrolyte is given in refs 1–3. Generally, the films were prepared in situ by a photoinitiated polymerization of a solution of (EG)₂₃DMA, (EG)₁₁DME, and LiCF₃SO₃ with Lucirin as photoinitiator at room temperature. The plasticizer content of the films was 50 wt % with respect to the mass of (EG)₂₃DMA. The salt content is related to the total content of oligo(ethylene glycol) groups both in the polymer and in the plasticizer. The film thickness varied between 100 and 300 μm .

DK. For the dielectric measurements, the samples were placed between two brass electrodes which were pressed together by a micrometer screw. A Solartron frequency response analyzer (FRA1260) was used in combination with a nitrogen gas heating system to control the temperature.

The measurements involve a temperature range from -100 to 100 °C and 10^{-2} to 10^7 Hz, which should be sufficient to investigate relaxation phenomena, conductivity, and dielectric permittivity.

Because of the great number of different kinds of dipoles in gel electrolytes and the multicomponent character of the materials, we started the investigations with the neat polymer P(EG)₂₃DMA, and then a plasticized film was measured followed by samples containing different contents of salt.

PFG-NMR Measurements. ¹H, ¹⁹F, and ⁷Li PFG-NMR experiments were carried out with a home-built spectrometer FEGRIS 400 (with a proton resonance frequency of 400 MHz) as described in refs 25–27 to measure the self-diffusion coefficients D of the plasticizer, the anions, and the cations in the gel electrolyte and in its liquid electrolyte as well as D of the neat plasticizer by ¹H PFG-NMR, respectively.

The stimulated echo pulse sequence $\pi/2 - \tau - \pi/2 - t - \pi/2 - \tau - \text{echo}$ was used (with $\tau \ll t$). Between the first and the second $\pi/2$ rf pulse and the third $\pi/2$ rf pulse and the echo two magnetic field gradients of duration δ and magnitude g were applied. In one experiment, δ and t were fixed and g was incremented from 0 to 25 T/m. The self-diffusivity D was calculated from the spin–echo attenuation $S_{\text{inc}}(q, t)$ due to the applied field gradients with the relation

$$S_{\text{inc}}(q, t) = \exp(-q^2 D t) \quad (16)$$

where $q = \gamma \delta g$ is a generalized scattering vector, with γ denoting the gyromagnetic ratio of the nucleus under study (¹H, ¹⁹F, or ⁷Li, respectively).

In every case, only one self-diffusion coefficient was observed. That means there exists no distribution of self-diffusion coefficients of the three species within experimental error. The time interval τ was always 3 ms; t was chosen between 10 and 100 ms and δ between 0.5 and 2 ms such that at the largest field gradient $g = 25$ T/m. The spin–echo was attenuated down to about 10%.

DSC. The thermal properties of the gel electrolytes were measured by the differential scanning calorimetry system DSC 220 C of Seiko Instruments in a temperature range from -100 to 150 °C with a heating rate of 10 K/min.

Electrochemical Measurements. Ac and dc measurements were carried out by means of a combination of a Solartron FRA 1255 and a Solartron ECI 1286.

Results

DSC. The cross-linked polymer P(EG)₂₃DMA is fully amorphous. The DSC thermogram shows one glass transition at -47 °C, only. The ends of the oligo(ethylene glycol) segments are fixed by the methacrylate units of the network. Therefore, they are not able to crystallize.

The neat plasticizer (EG)₁₁DME is a partially crystalline material; its thermogram contains a melting process with an onset at -9 °C (Table 1).

The addition of (EG)₁₁DME to the polymer decreases the T_g of the latter from -47 to -60 °C. With regard to previous studies of gel electrolytes on the basis of copolymers of oligo(ethylene glycol)_{*n*} methacrylates with acrylonitrile,^{1,15} fully amorphous films were expected, especially in the presence of

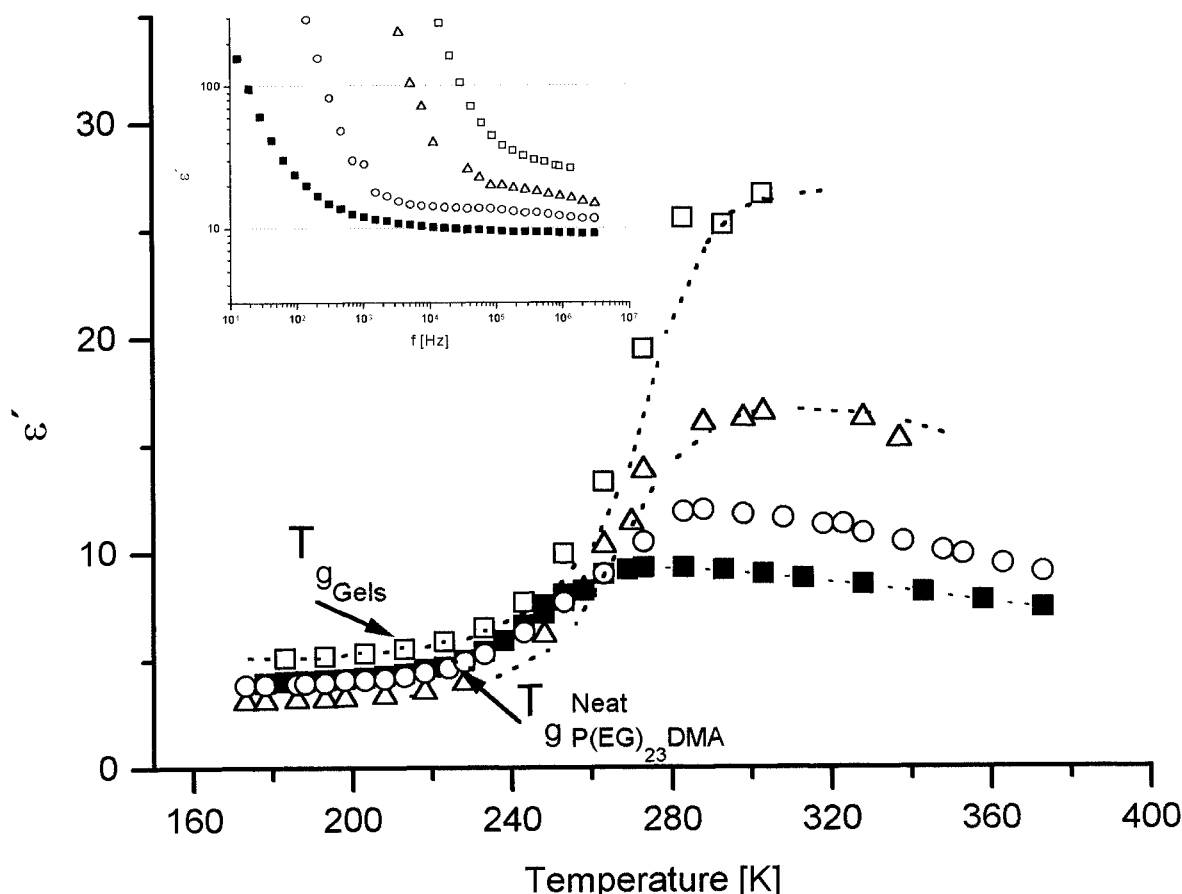


Figure 1. Real part of the dielectric permittivity in dependence on the temperature (at 1 MHz) and the frequency (at 298 K) of a gel electrolyte on the basis of P(EG)₂₃DMA with 50 wt % (EG)₁₁DME and LiCF₃SO₃, [EG]/[LiCF₃SO₃] = 75 Δ , [EG]/[LiCF₃SO₃] = 25 (\square), and the corresponding gel (\circ) and the polymer (\blacksquare) without salt.

the salt. However, the melting point of the plasticizer was always observed in the thermogram of the investigated gels.

The addition of salt to the plasticizer or to the gel leads to reduction of the degree of crystallinity of the samples indicated by a distinct decrease in the melting enthalpy of the plasticizer. The complexation of the cations hinders the oligo(ethylene glycol) units from crystallizing. Consequently, the gel electrolyte and the liquid electrolyte with the highest salt concentration, [EG]/[LiCF₃SO₃] = 25, have the lowest degree of crystallinity with respect to the melting enthalpy. The decrease of the degree of crystallinity is even indicated by the DSC thermograms of (EG)₁₁DME solutions. A glass transition (around -69 °C) was observed only in the presence of salt (Table 1).

An increase of T_g with increasing content of salt due to ionic cross-linking of the EG units via cation coordination as observed for nonplasticized polymer electrolytes^{18,28} did not occur in the case of the samples of Table 1.

Dielectric Response. *Dielectric Permittivity.* Figure 1 shows the permittivity, which reflects the ability of the polymer system to screen Coulomb interactions in dependence on the frequency at room temperature.

The plateau values for the real part of the dielectric response of the salt-free systems (the frequency response of ϵ' is given as an inset in Figure 1) are around 10 at room temperature. A value of this magnitude can be expected because of the high content of EG units (more than 80 wt %) and the amorphous character of the samples, because neat molten PEO has a permittivity of 8 (at 65.7 °C).¹⁹ The permittivity of PMMA is around 3, with a weak dependence on frequency and temperature.²⁹

TABLE 1: Results of DSC Investigations

sample	[EG]/ [LiCF ₃ SO ₃]	T_g [°C]	T_m^a [°C]	melting enthalpy [mJ/mg]
P(EG) ₂₃ DMA		-47		
solution of LiCF ₃ SO ₃ in (EG) ₁₁ DME			-9	161
	40	-69	-11	119
	30	-69	-14	99
	25	-68	-10	76
gel electrolyte from (EG) ₂₃ DMA with 50 wt % (EG) ₁₁ DME		-60	-12	76
	75	-61	-11	59
	25	-59	-16	47

^a Onset of the melting peak.

The plasticizing of P(EG)₂₃DMA with (EG)₁₁DME leads to a small, but clear increase in ϵ' at temperatures above the melting point of the plasticizer (Figure 1). Furthermore, an increase of the permittivity was observed due to the addition of the salt. The latter is in agreement with investigations of Fontanella¹⁹ and Gray¹⁸ et al. concerning the permittivity of salt-containing PEO or PPO systems. This behavior is most likely caused by changes in the average dipole moments or the polarizability of the solvent due to the dissolution of the salt.

In every case, the permittivity increases with decreasing frequency corresponding to the dielectric loss. This increase is very high and can partly be related to electrode polarization effects and the relatively high ionic conductivities of the samples.

As expected, ϵ' is relatively independent of the temperature and of the system studied at temperatures below T_g (Figure 1). The values are around 4. Wintersgill et al. determined an ϵ'

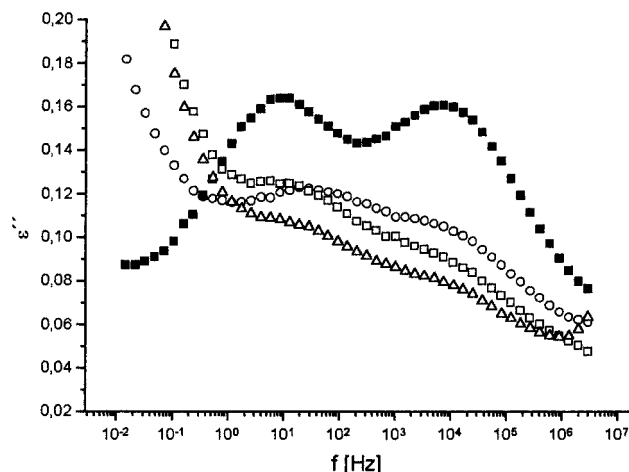


Figure 2. Dielectric loss in dependence on the frequency below the glass transition at 193 K of a gel electrolyte on the basis of P(EG)₂₃DMA with 50 wt % (EG)₁₁DME and LiCF₃SO₃, [EG]/[LiCF₃SO₃] = 75 (Δ), [EG]/[LiCF₃SO₃] = 25 (\square), and the corresponding gel (\circ) and polymer (\blacksquare) without salt.

value of approximately 2.9 for neat PEO at 5 K.³⁰ At temperatures higher than T_g (Figure 1) the permittivity increases, goes through a maximum between 270 and 290 K, and decreases with increasing temperature in both the salt-containing and the salt-free systems. This behavior is in agreement with the above-mentioned investigations of Wintersgill and Fontanella et al.^{19,30} and can be explained by changes of the conformation of the PEG chain with increasing temperature. Recent FT-IR spectroscopy studies by Bernson et al.^{31,32} of PEO systems containing La(CF₃SO₃)₃ indicate a change from gauche to trans conformation at the O—C—C—O dihedral angle of the PEO chain with increasing temperature. As a result, the PEO chains straighten out, the helical arrangement around coordinated cations is successively destroyed, and hence the ability of the PEO chain to coordinate cations decreases. Consequently, the ionic association in polymer electrolytes is enhanced with increasing temperature, which has been observed by Raman spectroscopic studies in the case of the investigated and other systems.^{4,33,34}

Dielectric Loss. Starting with 173 K two relaxation processes were observed in ϵ'' (Figure 2). The relaxation parameters can be fitted and described by the Havriliak–Negami function (eq 3) up to a temperature of approximately 200 K. The relaxation times at the peak maximum τ_{\max} and the dielectric strength $\Delta\epsilon$ of both processes (Figure 2) were determined.

The Arrhenius plots of the relaxation times at the peak maximum are shown in Figure 3. The differences between the values of the plasticized systems are low and within experimental error. The neat polymer seems to relax somewhat faster and with a higher dielectric strength. No clear dependencies on the content of salt were observed. The processes are not related to the glass transition with respect to the temperature range in which they take place and the Arrhenius-like temperature dependence of their dielectric relaxation rates.

The process with the lower activation energy (ca. 0.35 eV averaged over all values) (Figure 3) can be related to the γ relaxation of EG segments, i.e. to an amorphous transition involving the motion of very small segments of the polymer network.¹⁹ An activation energy of 0.33 eV for this process combined with an activation volume of 4 cm³/mol was described by Fontanella et al.^{19,30,35} for neat PEO ($M = 5 \times 10^6$ g/mol). The dielectric strength does not change during the investigated temperature range and is approximately 0.4 in the case of the plasticized systems and around 1 for the neat polymer.

The other process (Figures 2, 3) has a higher activation energy (ca. 0.6 eV) (Figure 3), but the dielectric strength is comparable with process 1. An assignment to the β relaxation of PEO can be ruled out because this process should take place at higher frequencies.^{18,19} Primarily, an assignment to the β relaxation of methacrylate groups was not expected in this temperature and frequency range, but it seems to be possible in consideration of the activation energy (Zeeb et al.³⁶ determined an activation energy of 0.67 eV for the β relaxation of unplasticized poly-(propyl methacrylate)) and considering the high inner and outer plastification of the samples.

In the case of the plasticized systems, the relaxation processes discussed are covered by the Maxwell–Wagner polarization at higher temperatures, as expected. For the neat polymer, this process can be neglected. The Maxwell–Wagner polarization characteristically shows a very high dielectric strength, which cannot be explained by the motion or rotation of molecule groups. The physical meaning of the Maxwell–Wagner polarization is not fully understood at present. Commonly, it is seen in connection with the polarization at interlayers and phase boundaries within the sample. We do not discuss this effect further, but it was necessary to treat the Maxwell–Wagner relaxation like a conductivity contribution to calculate the Havriliak–Negami parameter for the relaxation processes.

The high-temperature behavior of the dielectric loss is dominated by the conductivity in all systems studied. Therefore, only the dc conductivity (Figure 4) was fitted and plotted at $T > 250$ K for salt-containing plasticized systems and at $T > 280$ K for systems without salt. In the case of the salt-containing systems, polarization effects were observed more and more with decreasing frequency at the high-temperature end of the measurements.

Conductivity. A comparison of the dc conductivities (Figure 4) (Havriliak–Negami fit, eq 3) of the neat polymer with the plasticized systems with and without salt demonstrates the influence of the mobility and the charge carrier number on the conductivity. The addition of the plasticizer results in a conductivity enhancement of 3 orders of magnitude. The addition of the salt is far less effective. Already at a salt content corresponding to [EG]/[LiCF₃SO₃] = 25 the maximum in conductivity is^{2,37} attained.

Unfortunately, the dc conductivities could be calculated by the Havriliak–Negami fit according to eq 3 only in a limited temperature range due to the overlapping of the conductivity with the Maxwell–Wagner polarization. The data cannot successfully be fitted by the VTF or the WLF equation because of the melting of crystalline parts of the plasticizer as observed by DSC (Table 1).

Below the glass transition temperature T_g (Figures 5d and 6), the investigated samples behave very similar. The conductivity spectra are only slightly temperature dependent, comparable to the behavior described for other ion-containing polymers.^{38–40} The plots in the $\log \sigma'/\log f$ diagram (Figure 5) overlap and are nearly linear (deviations arise from the relaxation processes discussed). The conductivity is proportional to ω^{-s} , where s is approximately 0.95. An onset of the ionic mobility above the glass transition of the gel has already been reported by Stallworth et al.⁴¹ In the case of PPO–LiCF₃SO₃ systems, Wintersgill et al.¹⁹ could fit conductivity and data for the α relaxation with the same VTF equation and concluded that the ion transport mechanism is dominated by large-scale segmental motion of the polymer chains.

For temperatures above the glass transition, the conductivity spectra in dependence on the frequency can be divided into two

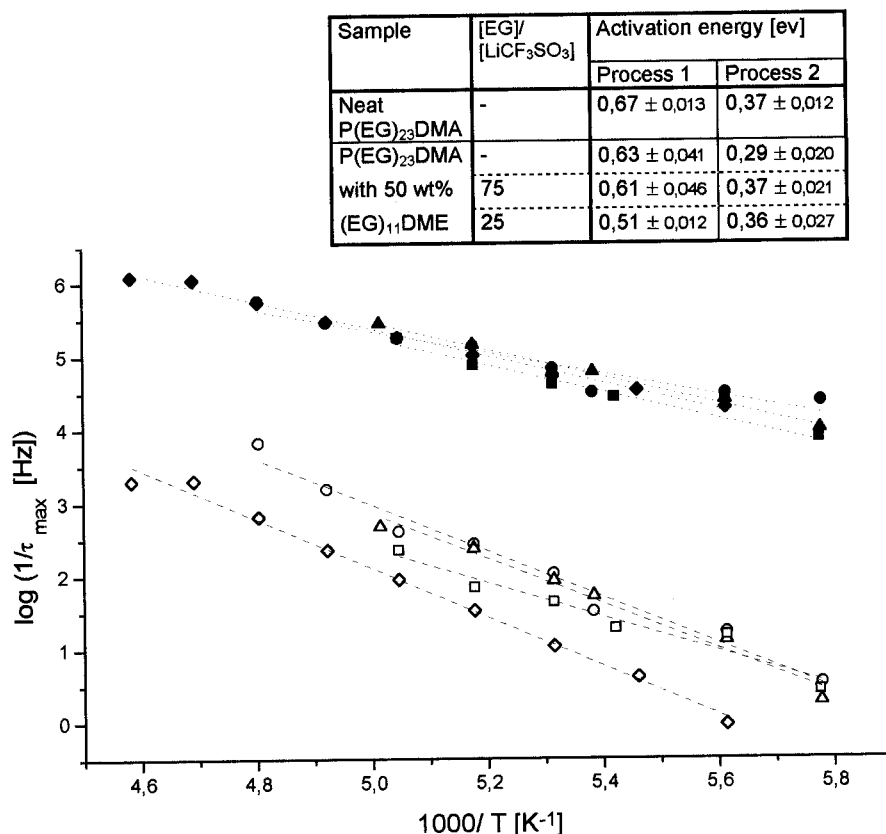


Figure 3. Relaxation time at the peak maximum of the two processes observed below the glass transition (process 1, open symbols; process 2, closed symbols) in dependence on temperature for a gel electrolyte on the basis of P(EG)₂₃DMA with 50 wt % (EG)₁₁DME and LiCF₃SO₃, [EG]/[LiCF₃SO₃] = 75 (△,▲) [EG]/[LiCF₃SO₃] = 25 (□,■), and the corresponding gel (○,●) and the polymer (◇,◆) without salt.

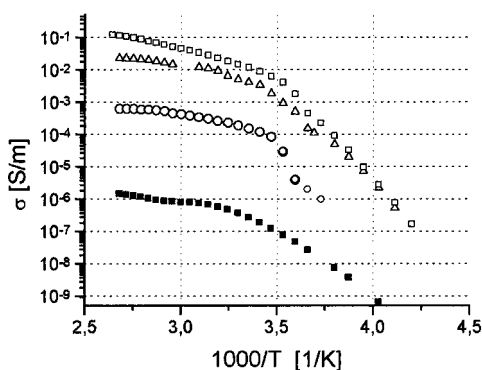


Figure 4. Dc conductivity fitted with help of the Havriliak–Negami eq 3 for a gel electrolyte on the basis of P(EG)₂₃DMA with 50 wt % (EG)₁₁DME and LiCF₃SO₃, [EG]/[LiCF₃SO₃] = 75 (△), [EG]/[LiCF₃SO₃] = 25 (□) and the corresponding gel (○) and the polymer (■) without salt.

regions (Figure 5c): a low-frequency plateau and a dispersion region in which the conductivity follows a power law. This behavior is commonly observed for ion-conducting polymers:^{38–40} From the point of theory a third region, the Funke plateau, which arises from hopping conduction, should be expected at high frequencies. According to a recent discussion of the conductivity spectra of solid ionic conductors by Liu,⁴² the high-frequency plateau exists only under certain circumstances. The low-frequency plateau of the conductivity is dominated by space charge relaxation arising from the diffusion of ions. Induced dipole relaxation is the main contribution to the high-frequency region.

For temperatures above the melting point of the plasticizer the frequency dependence of the conductivity spectra essentially disappears (Figures 5a and 6). Deviations from the curvature

at the low-frequency side can be explained by electrode polarization effects and/or arise from Maxwell–Wagner relaxation, especially at intermediate frequencies (Figure 5b).

Self-Diffusion Coefficients. The self-diffusion coefficients of the plasticizer and the charge carriers of the investigated gel electrolyte systems are plotted in Figure 7 together with the values of the liquid electrolyte and the self-diffusion coefficient of the neat plasticizer. The measurement of the plasticizer diffusion was extended to 0 °C. A significant decrease in diffusivity was observed below 10 °C due to the crystallization of the plasticizer. The temperature dependence of the self-diffusion coefficients in the temperature range between 25 and 80 °C can be described by the Arrhenius equation with good correlation. The activation energies are summarized in Table 2.

The addition of LiCF₃SO₃ to (EG)₁₁DME reduces the self-diffusivity of the latter due to the coordination of cations (Figure 7). The anion diffusivity is comparable with the plasticizer diffusivity in the liquid electrolyte system. The cationic self-diffusion coefficients are distinctly lower. The cationic transference numbers calculated via $t^+ = D_{\text{exp}}(\text{Li})/(D_{\text{exp}}(\text{Li}) + D_{\text{exp}}(\text{F}))$ are between 0.36 and 0.42 depending on the temperature.⁵

Naturally, the values of the self-diffusion coefficients of the plasticizer and the charge carriers in the gel electrolyte are further reduced as compared with the liquid electrolyte due to the additional interaction with the polymer, and distinctly higher activation energies were calculated (Table 2). Compared to the liquid electrolyte system, the anion diffusion is slower than the diffusion of the plasticizer. The ratio between the anion and cation self-diffusion coefficients is essentially unchanged. The values of the cationic transference numbers t^+ (calculated as above) are only insignificantly smaller, with values between

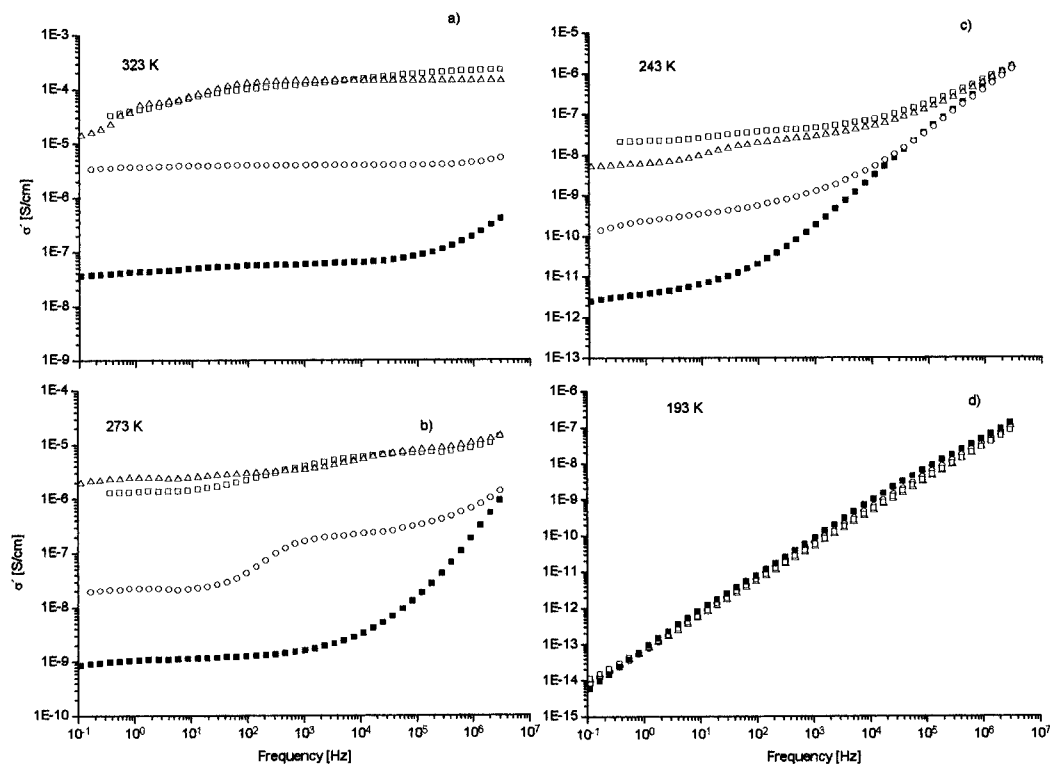


Figure 5. Real part of the conductivity at different temperatures in dependence on the frequency for a gel electrolyte on the basis of P(EG)₂₃DMA with 50 wt % (EG)₁₁DME and LiCF₃SO₃, [EG]/[LiCF₃SO₃] = 75 (Δ), [EG]/[LiCF₃SO₃] = 25 (□) and the corresponding gel (○) and the polymer (■) without salt.

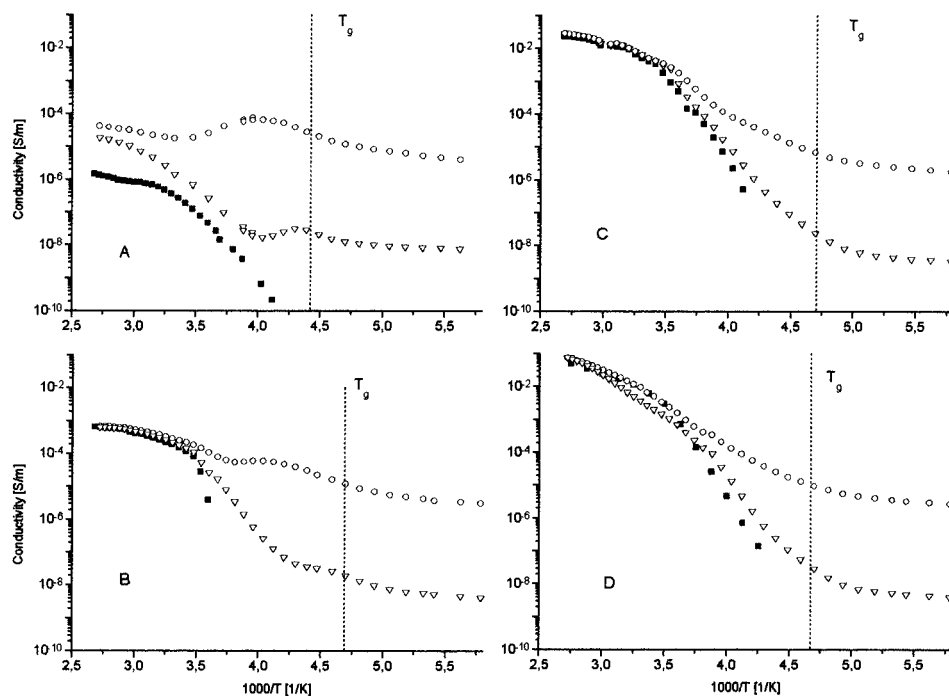


Figure 6. Dc conductivity (■) compared with the real part of the conductivity at 1 MHz (○) and 1 kHz (▽) in dependence on the temperature. Gel electrolyte on the basis of P(EG)₂₃DMA with 50 wt % (EG)₁₁DME and LiCF₃SO₃, [EG]/[LiCF₃SO₃] = 75 (C), [EG]/[LiCF₃SO₃] = 25 (D), and the corresponding gel (B) and polymer (A) without salt.

0.35 and 0.38, than those of the liquid electrolyte system, indicating the distribution of cations between the polymer and the plasticizer. The determination of t^+ by the steady-state current technique⁵ resulted in only slightly higher values.

The deviation from the Nernst–Einstein equation as expressed by the Haven ratio (Figure 8) increases with increasing temperature for both systems, probably due to the enhanced ionic association observed by Raman spectroscopic investigations.^{4,33}

These indicate furthermore that higher ionic associates than ion pairs can be neglected in these electrolytes.

Interestingly, the deviation from the Nernst–Einstein equation was found to be distinctly lower for the gel electrolyte than for the liquid electrolyte (Figure 8), although the latter system shows the higher content of free anions.³³ A similar behavior was described by Clericuzio et al. concerning the Haven ratio for polyether-based networks containing tetraglyme.¹⁰ As discussed

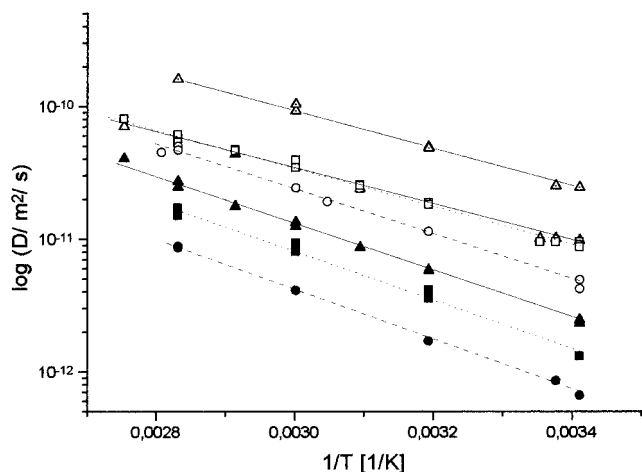


Figure 7. Temperature dependence of the self-diffusion coefficients of neat (EG)₁₁DME (Δ) in comparison with its diffusivity and the diffusivity of the charge carriers in a liquid electrolyte (EG)₁₁DME with 0.72 mol/kg LiCF₃SO₃ (open symbols) and in a gel electrolyte from (EG)₂₃DMA with 50 wt % (EG)₁₁DME and 0.74 mol/kg LiCF₃SO₃ (closed symbols), $D_{\text{plasticizer}}$ (Δ), D_{anion} (□), D_{cation} (○).

TABLE 2: Activation Energies Calculated from the Temperature Dependence of the Self-Diffusion Coefficients of the Charge Carriers and Plasticizer and the dc Conductivity (25–80 °C) in a Gel Electrolyte from (EG)₂₃DMA with 50 wt % (EG)₁₁DME and [EG]/[LiCF₃SO₃] = 25 and Its Corresponding Liquid Electrolyte

sample		activation energy [eV]
neat (EG) ₁₁ DME	$D_{\text{plasticizer}}$	0.28 ± 0.01
solution of LiCF ₃ SO ₃ in (EG) ₁₁ DME, [EG]/[LiCF ₃ SO ₃] = 25	fluidity (1/η)	0.19 ± 0.01
	$D_{\text{plasticizer}}$	0.27 ± 0.02
	D_{anion}	0.29 ± 0.02
	D_{cation}	0.33 ± 0.04
	conductivity	0.25 ± 0.01
gel electrolyte from (EG) ₂₃ DMA with 50 wt % (EG) ₁₁ DME and [EG]/[LiCF ₃ SO ₃] = 25	$D_{\text{plasticizer}}$	0.34 ± 0.01
	D_{anion}	0.36 ± 0.03
	D_{cation}	0.39 ± 0.04
	conductivity	0.33 ± 0.04

above, increasing deviations from the Nernst–Einstein equation with enhanced contribution of species that do not take part in the conductivity to the overall diffusivity may be explained either by enlarged concentration c_b or by enhanced diffusivity D_b of the bound species. That means if the lower values of the Haven ratio in the gel electrolyte system cannot be explained with diminished ionic association, they should indicate a decreased diffusivity of the bound species (not involved in the conductivity) compared to the free ionic species.

Conclusion

The dielectric response of gel electrolytes on the basis of P(EG)₂₃DMA plasticized with (EG)₁₁DME depends on the salt content of the samples and on the mobility of the polymer chains as the carriers of the dipoles.

The enhancement in polymer mobility due to the addition of the plasticizer leads to a slight increase in permittivity and to a distinctly higher conductivity. Below the glass transition, i.e. in a temperature range with restricted polymer mobility, all samples coincide widely in their dielectric response independent of their content of salt or plasticizer. The behavior above the glass transition is characterized by an increasing permittivity and conductivity. The conductivity is strongly frequency dependent in this temperature range. For temperatures higher than 25 °C, after the melting of the plasticizer, the frequency

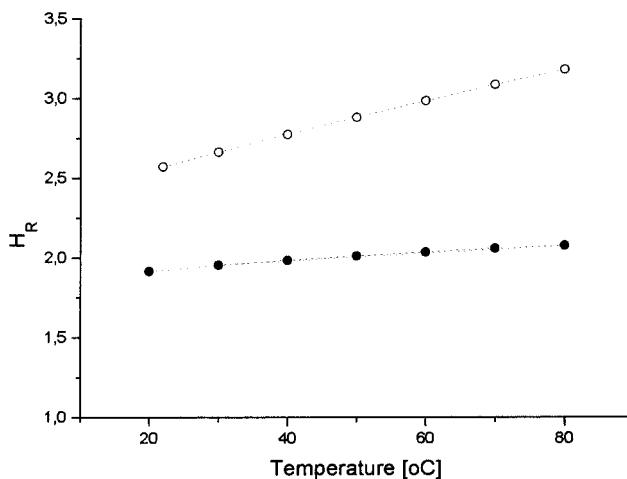


Figure 8. Haven ratio $H_R = D_{\text{exp}}/D_\sigma$ in dependence on the temperature for the gel electrolyte on the basis of (EG)₂₃DMA with 50 wt % (EG)₁₁DME and 0.74 mol/kg LiCF₃SO₃ (●) and its liquid electrolyte (○).

dependence of the conductivity disappears in the case of the plasticized samples. The permittivity goes through a maximum at room temperature and decreases with further temperature enhancement with respect to an increase in ionic aggregation indicated by growing deviations from the Nernst–Einstein relationship. These deviations expressed in terms of the Haven ratio are referred to bound species that contribute to the overall diffusivity but do not take part in the conductivity. The observed deviations may result from an enlarged content c_b of these species or by an enhancement of their self-diffusivity D_b .

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