

Dielectrics Newsletter

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I. Albinsson, H. Eliasson and B.-E. Mellander

Dielectric Properties of Polymer Electrolytes

Introduction

Polymer electrolytes have been the subject of many investigations concerning ionic conductivity, shear viscosity, structure and vibrational properties just to mention a few. The electrical measurements are most often done in order to determine the ionic conductivity by analysing the complex impedance over a wide frequency range. Some of the most commonly described polymer electrolytes consist of LiCF_3SO_3 , NaCF_3SO_3 , KCF_3SO_3 or $\text{NH}_4\text{CF}_3\text{SO}_3$ dissolved in polymers such as poly(ethylene oxide), PEO, or poly(propylene oxide), PPO. The

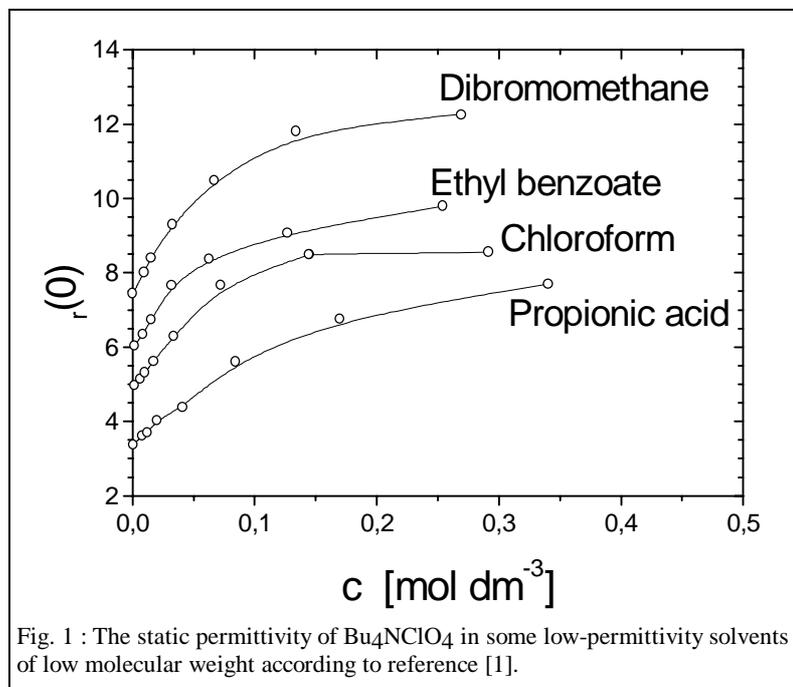


Fig. 1 : The static permittivity of Bu_4NClO_4 in some low-permittivity solvents of low molecular weight according to reference [1].

ion transport in these complex systems is dependent on a number of variables whereof the flexibility of the polymer chain is expected to be rate determining for the mobility

of the charge carriers.

Information about dipoles in polymer electrolytes may be obtained from an analysis of the complex permittivity. A number of dipolar relaxations may be of interest such as segmental and even larger unit relaxations of the polymer itself and relaxations due to the complexation with the salt, e.g. cation-anion pairs or larger aggregates. The dielectric properties have, however, not been as extensively analysed as other properties. This is due to a fundamental difficulty when investigating the dielectric properties of electrolytes, especially at low frequencies, namely the influence of ion conduction. The higher the ionic conductivity, the larger is the contribution to the permittivity from the electrochemical double layer at the electrodes. This

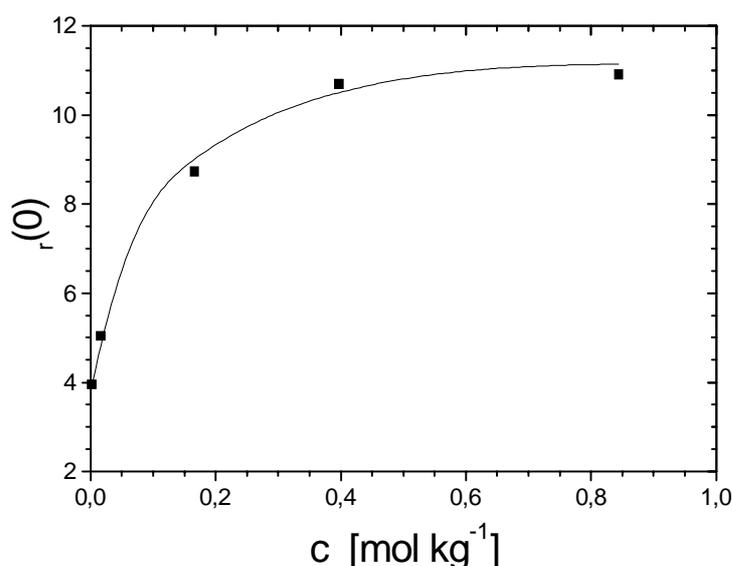


Fig. 2 : The static permittivity of AgCF_3SO_3 dissolved in PPG4000.

contribution often makes it difficult or impossible to detect dielectric relaxations. An extrapolated ϵ_r towards infinitely low frequency may still sometimes be found under the assumption that no other relaxations occur at lower frequencies than the frequency from which the extrapolation is made.

Dielectric Studies of Ion Association

In high permittivity liquid electrolytes, for example water solutions, ϵ_r decreases with increasing salt concentration. In these solutions the dipoles of the solvent are symmetrically bound to the dissociated ions in the solvation sheath. Thus, the dipoles in the solvation sheath have not the ability to align with an external electric field, and therefore, as the concentration of dissociated ions increases more solvent dipoles are hindered from aligning, and ϵ_r is decreasing.

In low-permittivity solvents of low molecular weight, it is well known that a salt is not completely solvated, that is, dissociated ions, ion pairs, triplets and larger aggregates exist in equilibrium with each other [1]. For these

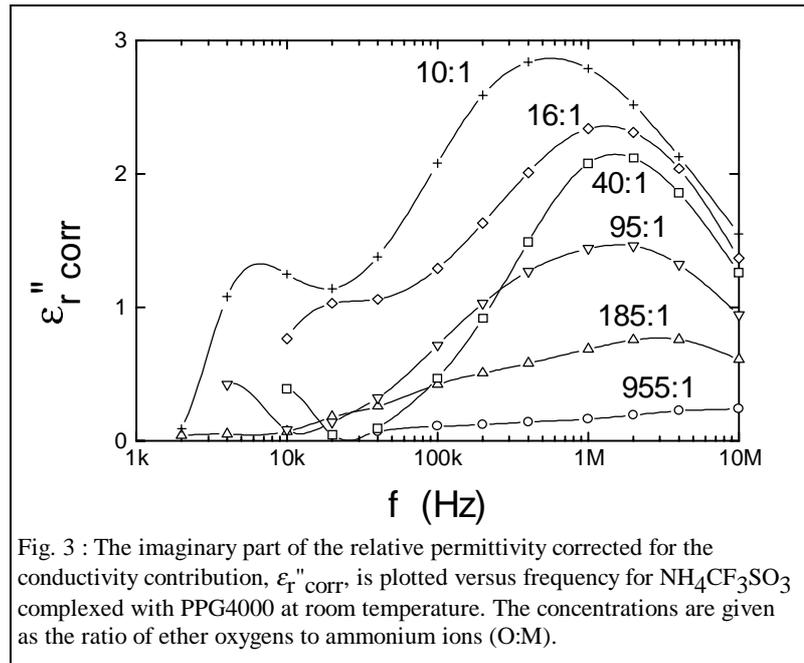


Fig. 3 : The imaginary part of the relative permittivity corrected for the conductivity contribution, $\epsilon_r'' \text{corr}$, is plotted versus frequency for $\text{NH}_4\text{CF}_3\text{SO}_3$ complexed with PPG4000 at room temperature. The concentrations are given as the ratio of ether oxygens to ammonium ions (O:M).

electrolytes an increase in ϵ_r with increasing concentration of salt has been attributed to an increase in the concentration of ion pairs with large dipole moments, see Figure 1. We have measured the complex permittivity for a number of different polymer electrolytes [2-5]. A polymer electrolyte can in some respects be compared to a low permittivity liquid solution [3,5], see Figure 2. With the same assumption for polymer electrolytes as for low-permittivity solutions,

the initial increase in ϵ_r with increasing dipole concentration can be related to the dipole moment of the ion pairs [1]. If we introduce our measured values from Figure 2 we can obtain the dipole moment for AgCF_3SO_3 dissolved in poly(propylene glycol) of molecular weight 4000, PPG4000. Since the dipole moment of the ion pair,

$$\mu_2 = aQ \quad (1)$$

where Q is the charge, we can relate a to the distance of separation between the cation and the anion of the ion pair. Using the calculated dipole moments from Figure 2 and the references [3,4,6] we obtain an estimation of the interionic separation of the ion pairs, see Table 1. Also in the case of polymer electrolytes, the results support the interpretation that the increase in ϵ_r with increasing concentration of salt is mainly due to ion pairs.

Now, assume that the main part of the anion charge is located at the center of the three oxygen atoms, and that associated cations are bound to only one anion oxygen at the time. This suggests that the charge separation of the ion pair, a , would be of the order of the sum of one oxygen diameter and the cation

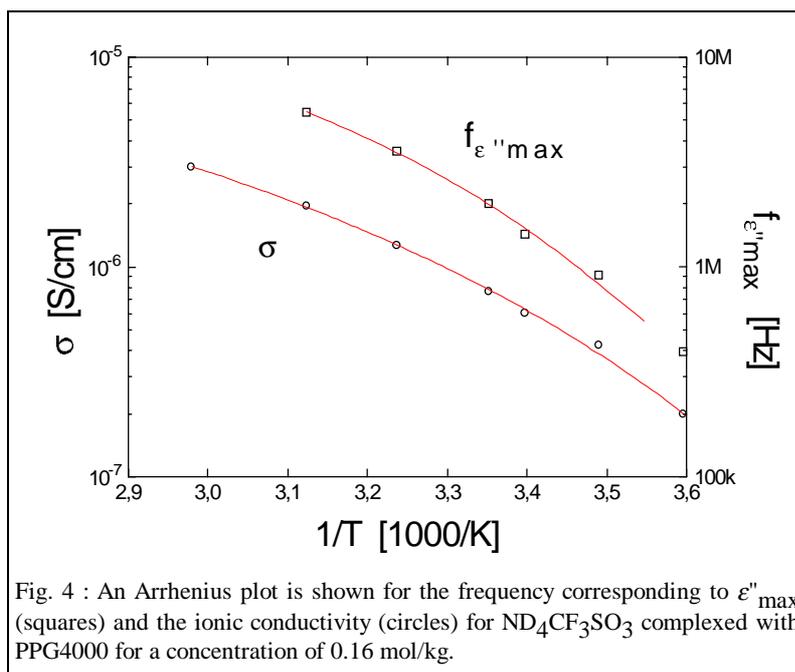


Fig. 4 : An Arrhenius plot is shown for the frequency corresponding to $\epsilon_r'' \text{max}$ (squares) and the ionic conductivity (circles) for $\text{ND}_4\text{CF}_3\text{SO}_3$ complexed with PPG4000 for a concentration of 0.16 mol/kg.

	Estimated separation	Calculated separation from eq. (1)
LiCF ₃ SO ₃	2.6	2.8
NH ₄ CF ₃ SO ₃	3	3.2
ND ₄ CF ₃ SO ₃	3	3.2
AgCF ₃ SO ₃	3.3	~4.7

Tab. 1 : Cation-anion separation in an ion pair in PPG4000. The estimation is made assuming an oxygen radius of approximately 1 Å.

radius. The estimation in Table 1 implies that the ions of the pairs are in contact and not separated by a solvation sheath. For AgCF₃SO₃ the measured separation is uncertain due to small number of data points.

If we consider the ion pairs as being the major cause of the increase in the static permittivity with increasing concentration, it is reasonable to expect a dispersion to occur in a frequency range corresponding to the relaxing dipoles. In low-permittivity liquid solvents the ion pair relaxation is detected at frequencies of the order of one GHz [1,7]. The relaxation time is, as a first approximation, proportional to the viscosity of the solvent [7]. Since the viscosity of PPG4000 is about 1000 times higher than that of the liquid solvents [1], it is reasonable to expect that the relaxation due to ion pairs should occur at about one MHz. In Figure 3 the imaginary part of the relative permittivity corrected for the conductivity contribution, $\epsilon_r''_{\text{corr}}$, is plotted versus frequency for NH₄CF₃SO₃ complexed with PPG4000. The results show a concentration dependent peak around 1 MHz. The maximum in $\epsilon_r''_{\text{corr}}$ increases with increasing concentration, which confirms that the dielectric relaxation may be due to ion pairs. This peak has also been detected for AgCF₃SO₃ [4] while for LiCF₃SO₃ the peak frequency is outside our available frequency range.

In a simple picture, the ion pairs may be regarded as moving in a viscous surrounding. The frequency at ϵ''_{max} , $f_{\epsilon''_{\text{max}}}$, could then be a

measure of the local viscosity of the polymer. In our systems, the viscous surrounding of the ion pairs is the chain segments of the polymer; therefore the local viscosity is related to the segmental flexibility. Since the segmental flexibility is rate determining for the mobility of the charge carriers [8], $f_{\epsilon''_{\text{max}}}$ might be a probe of the mobility for the moving ions. For the polymer electrolyte in Figure 4 we find that $f_{\epsilon''_{\text{max}}}$ correlates to the ionic conductivity. Although the concentration of charge carriers is temperature dependent, an increase of the ionic mobility is the major cause of the conductivity increase with increasing temperature. Though, any deviation in slope from the conductivity can be related to a change in the concentration of charge carriers.

Conclusion

Other methods for estimating the segmental flexibility of polymer electrolytes at different concentrations of salt that have been discussed earlier, are to measure the glass transition temperature, T_g , or the shear viscosity, η . One disadvantage of using T_g for this purpose is that the glass transition normally occurs at temperatures of about 100°C below the actual temperatures where the segmental flexibility is to be measured. The disadvantage of using η is that it is a macroscopic parameter, which only, as a first approximation, can probe the local flexibility. Therefore, $f_{\epsilon''_{\text{max}}}$ may serve as a better method for probing the segmental flexibility.

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I. Albinsson, H. Eliasson and B.-E. Mellander
Department of Physics,
Chalmers University of Technology
and Göteborg University,
S-412 96 Göteborg, Sweden

Friedrich Kremer, Martin Arndt

On the Analysis of Dielectric Data in Terms of Relaxation Time Distribution Functions

Dielectric spectra are typically analysed by use of generalized relaxation functions:

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\Delta\varepsilon}{(1 + i\omega\tau)^\alpha}$$

such as the Havriliak-Negami-function ($\alpha \leq 1$, $\alpha\gamma \leq 1$), the Cole-Cole-function ($\alpha \leq 1$, $\gamma \leq 1$) or the Cole-Davidson-function ($\alpha \leq 1$, $\gamma \leq 1$). The Debye equation results with $\alpha = \gamma = 1$. All these relaxation functions (with the exception of the Debye-equation) are primarily of empirical character. From the generalized relaxation functions the corresponding relaxation time distribution $g(\log \tau)$ can be analytically deduced [1]. It is defined by the expressions:

$$\varepsilon' = \varepsilon_\infty + \Delta\varepsilon \int \frac{g(\log \tau)}{1 + \omega^2 \tau^2} d(\log \tau)$$

$$\varepsilon'' = +\Delta\varepsilon \int \frac{g(\log \tau) \omega \tau}{1 + \omega^2 \tau^2} d(\log \tau)$$

An alternative direct determination of $g(\log \tau)$ from the experimental dielectric spectra $\varepsilon^*(\omega)$ is numerically possible. These so called "ill-posed" problems can be solved according to the Tikhonov regularization algorithm [2,3]. The first attempt to apply regularization techniques [4] to the analysis of dielectric data uses the CONTIN procedure of Provencher [5]. A method with a significantly higher accuracy of fitting was introduced by Schäfer [6] using the self-consistency method of Hohnerkamp and Weese [7]. The algorithm is based on solving an integral equation.

To calculate $g(\log \tau)$ from the experimental data the following expanded least-squares expression

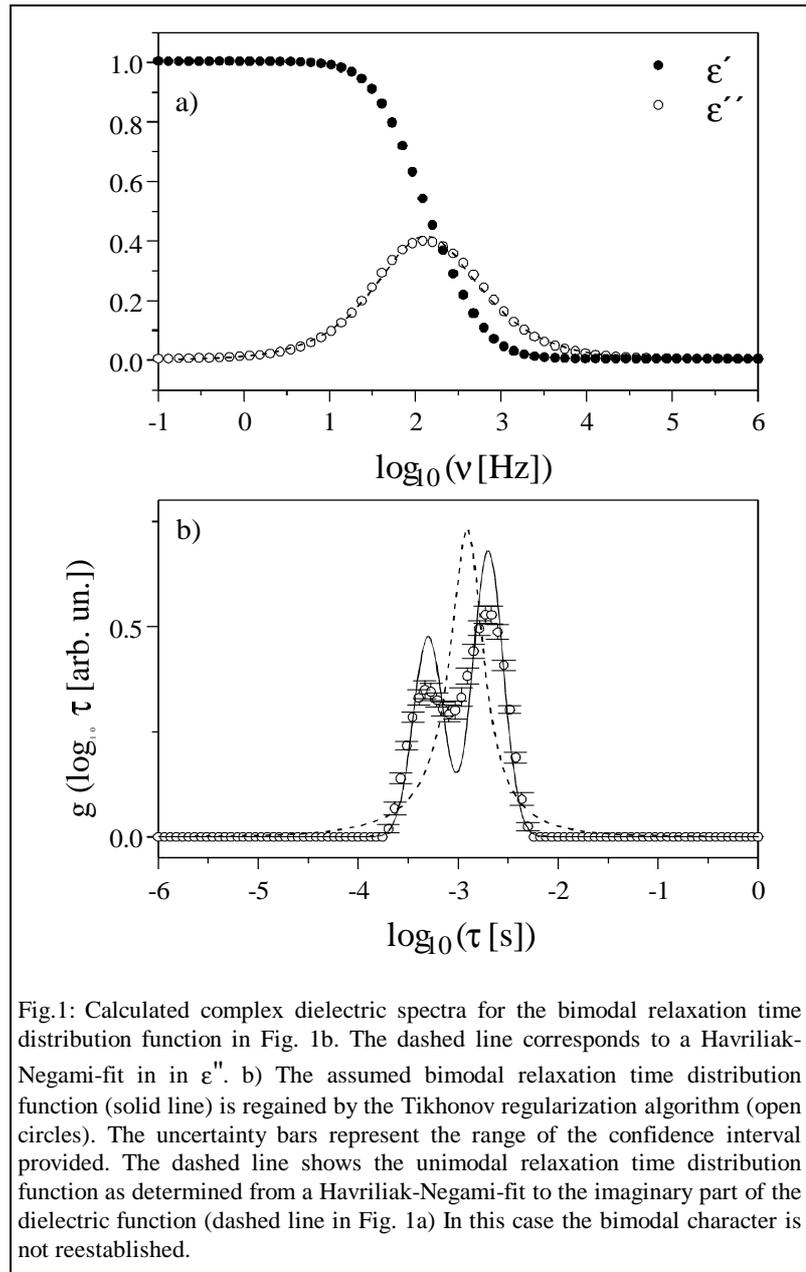


Fig.1: Calculated complex dielectric spectra for the bimodal relaxation time distribution function in Fig. 1b. The dashed line corresponds to a Havriliak-Negami-fit in ε'' . b) The assumed bimodal relaxation time distribution function (solid line) is regained by the Tikhonov regularization algorithm (open circles). The uncertainty bars represent the range of the confidence interval provided. The dashed line shows the unimodal relaxation time distribution function as determined from a Havriliak-Negami-fit to the imaginary part of the dielectric function (dashed line in Fig. 1a) In this case the bimodal character is not reestablished.

is minimized for a discrete set of experimental data

$$\varepsilon_j = (g(\log \tau), \varepsilon_\infty, \Delta\varepsilon) :$$

$$\Phi(g(\log \tau), \varepsilon_\infty, \Delta\varepsilon) =$$

$$\sum_i \left| \varepsilon_j^{\text{exp}} - \varepsilon_j^{\text{mod}} \right|^2 + \lambda \|g''(\log \tau)\|^2$$

The first term is the usual least-squares term which guarantees compatibility of the fit with the data. The second term introduces the regularization parameter λ that constrains the smoothness of $g(\log \tau)$ by controlling the second

derivative of $g(\log \tau)$. A good estimate for λ is essential for the quality of the solution. Too small values for λ result in artificial, physically meaningless structures in $g(\log \tau)$, while too large a λ tends to oversmooth the shape of $g(\log \tau)$ and to suppress information. Extensive simulation studies revealed that the algorithm used by Schäfer [6] is stable with respect to noise, provides excellent resolution of multiple relaxation processes, and extracts line shapes closely approximating the "true" $g(\log \tau)$.

In Fig. 1a,b the two methods to determine the relaxation time distribution function are compared. From the bimodal relaxation time distribution function (solid line in Fig. 1b) the complex dielectric spectrum in Fig. 1a is calculated (open and closed circles in Fig 1a). A fit (in ϵ'') using the Havriliak-Negami-function describes the experimental data well (within limits of $\pm 4\%$ of relative accuracy). The fit delivers an unimodal relaxation time distribution function (dashed line in Fig. 1b). In contrast the Tikhonov regularization algorithm regains the bimodal character of the assumed relaxation time distribution.

As a second example an asymmetric multimodal distribution with four Gaussian-broadened peaks is shown in Fig. 2 (b) and the corresponding complex spectrum in Fig. 2 (a). The discrete points in Fig. 2(b) show how well the calculated distributions reproduce the original "true" $g(\log \tau)$, and the physical interpretation is now possible in the τ domain.

The resolution and the ability to extract the true line shape of the algorithm improve as the noise is reduced and the number of sampled frequencies is increased. The choice of the frequency window does not critically influence the resolution as long as all processes are largely in the sampled region. A detailed analysis and a comparison between the two approaches is in preparation [8].

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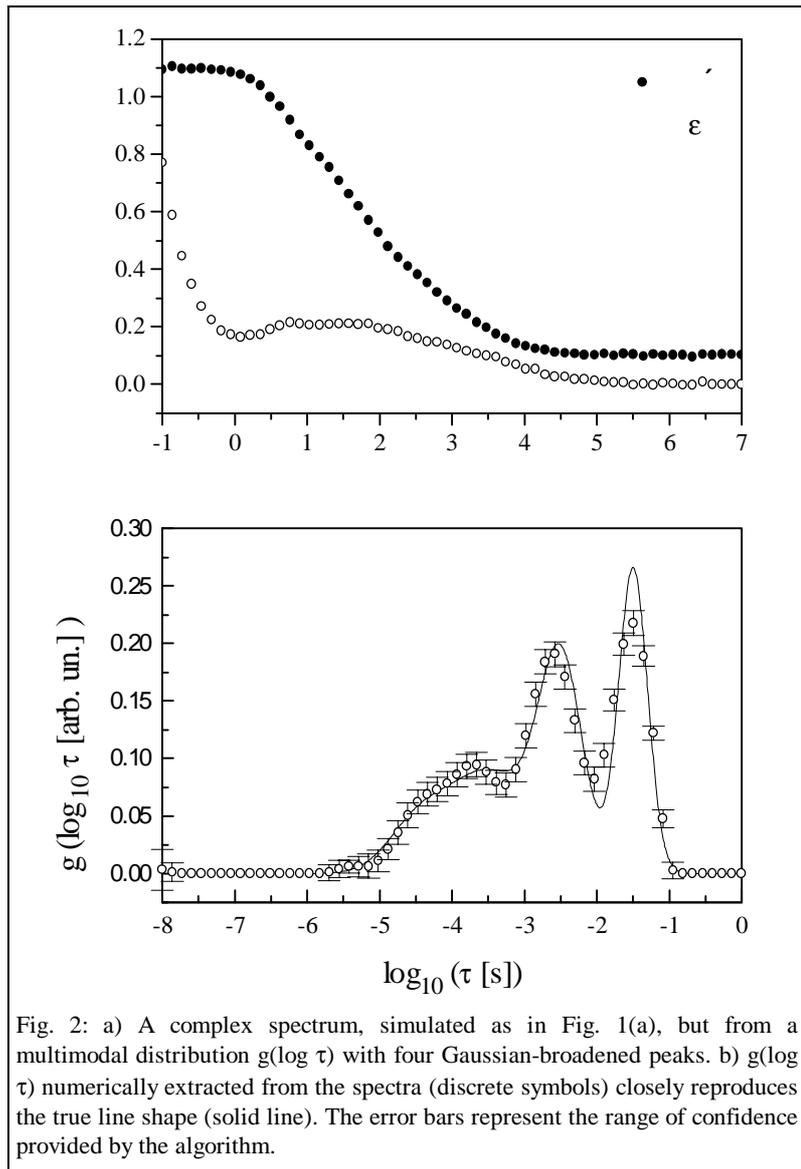


Fig. 2: a) A complex spectrum, simulated as in Fig. 1(a), but from a multimodal distribution $g(\log \tau)$ with four Gaussian-broadened peaks. b) $g(\log \tau)$ numerically extracted from the spectra (discrete symbols) closely reproduces the true line shape (solid line). The error bars represent the range of confidence provided by the algorithm.

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For question concerning regularization techniques contact: Dr. Harmut Schäfer, Universität Leipzig, Fakultät für Physik,

Linnéstr.5, D-04103 Leipzig, e-mail:

schaefer@tirol.exphysik.uni-leipzig.de

Prof. Dr. Friedrich Kremer, Dipl. Phys. Martin Arndt
Universität Leipzig, Linnéstr.5,
D-04103 Leipzig Germany

Martin Arndt

Dielectric and Mechanical Relaxation in Materials

by S. Havriliak, Jr. and S.J. Havriliak

This book describes dielectric, mechanical and viscoelastic relaxation in all types of materials, especially in polymers. All three phenomena are treated as jumping process. Through the use of these mechanisms, the relaxation phenomena are correlated to molecular motions. Dielectric and viscoelastic processes are applied to show how molecules move in small stress fields, i.e. electrical or mechanical fields. These jumping mechanisms are also applied to large stress fields to develop a molecular picture for important commercial properties of polymers such as tensile yielding and impact resistance.

The objective of this book is met by combining the results from a number of important fields or disciplines in physical science and statistics and applying them to the way materials in general and polymers specifically react when subjected to small and large forces such as those physically distorting or damaging macroscopic objects. - The use of physical intuition, rather than "statistical jargon" makes the book readable to a wide ranging audience, such as polymer and materials scientist, bio-physicists, colloid scientists, etc.

Dipl. Phys. Martin Arndt
Universität Leipzig, Linnéstr.5,
D-04103 Leipzig Germany

Gerhard Schaumburg

New Developments by Novocontrol

WinDETA and WinFIT Software Available for MS-Windows 95

The Novocontrol software packages WinDETA and WinFIT are now available for the MS-Windows95 operating system as 32 bit versions. Advantages compared to the 16 bit versions are long file names and shorter calculation times

e.g. for curve fitting procedures.

WinDETA supports ten of the most convenient impedance analyzers for dielectric measurements and several temperature controllers. It performs automatically calibrations procedures for the sample cells and can do dielectric and magnetic measurements up to four dimensions depending on frequency, temperature, dc-bias and time. The basic dielectric parameters, like complex dielectric function, impedance etc., are evaluated and displayed graphically in two and three dimensional representation.

WinFIT supports data manipulation and non linear curve fitting with the Havriliak Negami, Cole Davidson, Cole Cole, Debye, Williams Landel Ferry and Vogel Fulcher functions. In addition, the data are transformed from the frequency domain to the time domain and the relaxation time distribution is calculated. Arbitrary RLC component networks and arbitrary complex mathematical expressions can be simulated and fitted to the measured data.

Temperature Controlled Magnetic Material Measurements in the RF Regime

Novocontrol offers now in addition to dielectric- and impedance measurements magnetic material measurements. For this purpose, the Novocontrol dielectric sample cell is replaced by a magnetic cell. It is mounted at the RF extension line of the Novocontrol BDS 6000 RF system. In this set-up, the cell is thermally isolated from the impedance analyzer input.

The BDS 6000 system is based on the Hewlett Packard 4291A impedance analyzer and operates between 1MHz and 1.8GHz. Temperature control is available either with the QUATRO Cryosystem (-160°C .. 450°C,

0.01° stability) or with the Novotherm system (ambient .. 400°C, 0.1° stability).

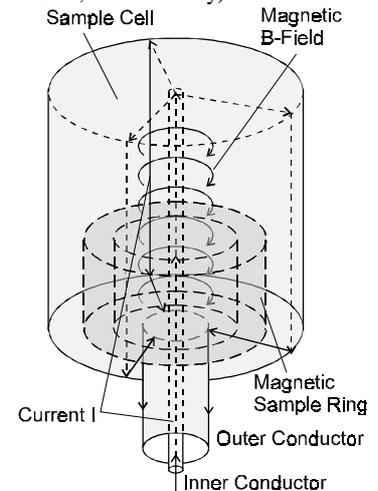


Fig. 1 : Principle of the sample cell for magnetic material measurements.

The sample must have the geometry of a cylindrical ring. It is placed centred in the magnetic cell as shown in fig. 1. If the sample cell is completely filled by the sample material, the magnetic permeability

$$\mu^* = \mu' - j\mu'' \quad (1)$$

of the sample material can be calculated from the complex sample inductivity by

$$\mu^* = \frac{L^*}{L_0}; \quad L^* = j\omega Z^* \quad (2)$$

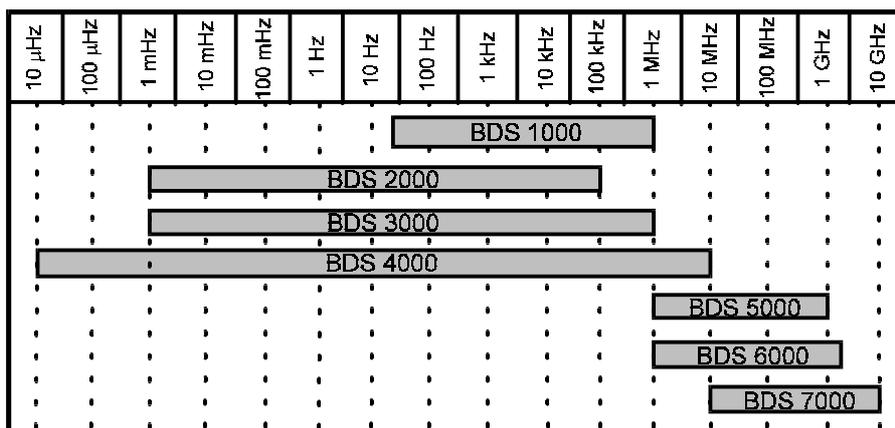
(L_0 : empty cell inductivity, $\omega=2\pi/\text{frequency}$, $j^2=-1$, Z^* : measured sample cell impedance)

In practice, the sample material must not completely fill the cell. In this case the inductivity of the not occupied cell volume is subtracted from the measured impedance in eqn. (2).

Magnetic material properties can also be determined under computer control with or without temperature control as these measurements are available as an option of the Novocontrol standard software WinDETA.

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