

# Dielectrics Newsletter

Scientific newsletter for dielectric spectroscopy

Issue march 1995

Dr. Ulrich Simon

## Impedance Spectroscopy on Ligand Stabilized Metal Clusters

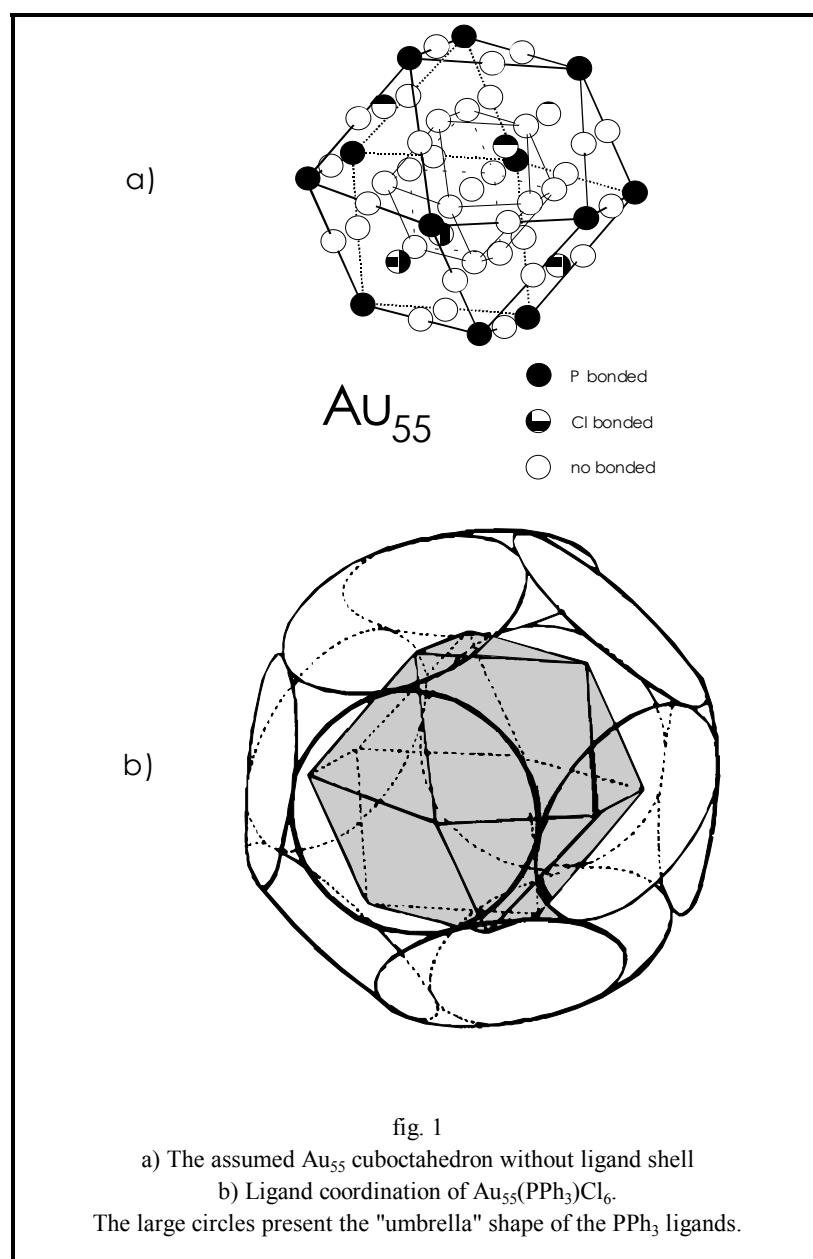
Impedance Spectroscopy (IS) or Dielectric Spectroscopy has become an important method of characterisation in different fields of research and especially in the broad field of materials research /1/. In this paper it is reported about the use of IS to characterize the electronic properties of ligand stabilized metal clusters with respect to possible applications of these materials for a new generation of microelectronic devices operations with single electrons. This field is called "Single Electron Locie" (SEL) or "Single Electronics" (SE).

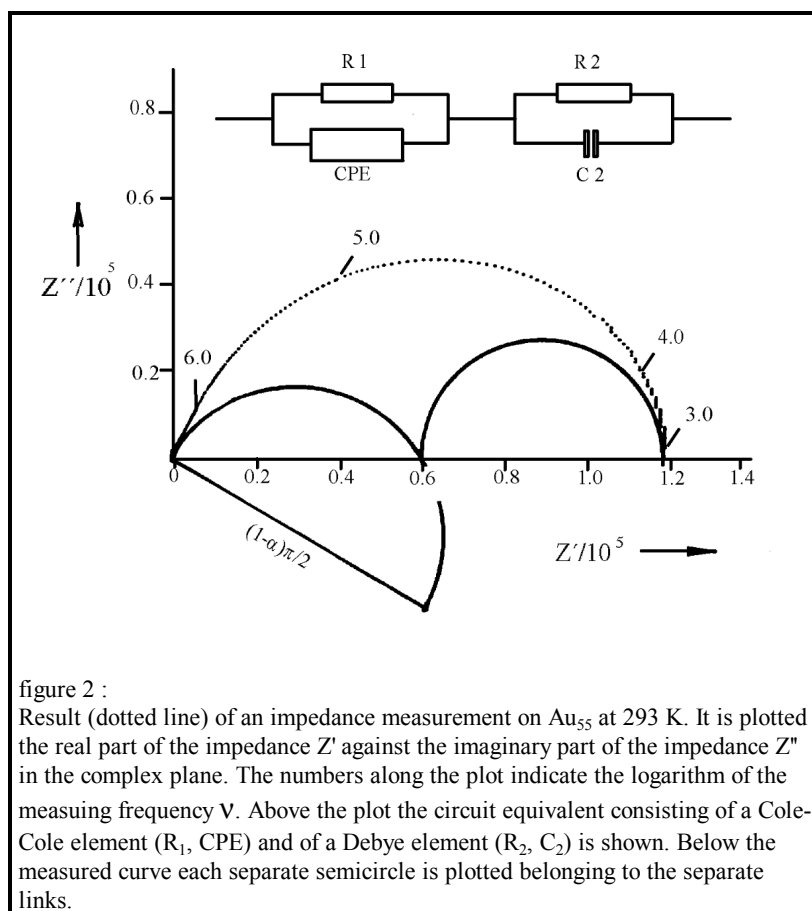
Metal clusters are extremely small solids in the range of few nanometers and they consist of only few single up to few hundred metal atoms. Several methods are known /2/ to synthesize such small solids. Generally naked or bare metal clusters, which can be synthesized by molecular beam techniques or matrix techniques, have a very short life time due to their high reactivity and they reveal a more or less broad size distribution. So preferably ligand stabilized metal clusters, which can be prepared by colloid-chemical techniques are ideal objects to study the properties of uniform particles since here the problem of size distribution has partially been solved. In these cluster types the organic ligand shell takes over the task of protection and prevents to the metal clusters from coalescence to bulk material. In arrangements of these clusters, like in crystals or pressed pellets, the ligand

shell acts like a "dielectric spacer" between neighboring clusters.

One example for such a small metal cluster is the  $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$  - Cluster (in the following called  $\text{Au}_{55}$ ), first synthesized by Schmid et al. /3/. It consist of 55 gold atoms, which are in a dense packed arrangement forming a

body of a roughly spherical shape with an average diameter of 1.4 nm. This metal core is surrounded by 12  $\text{PPh}_3$  - ligands that protect the cluster with their "umbrella" shape (see figure 1). In addition 6 Cl - ligands are connected to the gold cluster surface. The total diameter including the





ligand shell is approx. 2.1 nm.

Since the availability of such small solids an increasing number of research groups is engaged to investigate the transition from the molecule to the solid state. In this range of transition, when a metal particle, initially having bulk properties, is reduced in size to a few hundred or dozen of atoms, the physical properties change dramatically, i.e. conductivity, magnetism, etc. begin to disappear. Then the physical properties are mainly determined by quantum mechanical effects and therefore clusters in this size regime are called "Quantum Dots" or "Q-particles".

Beside the manifold of different questions in the basic research for the microelectronics one question is of major importance: What are the physical limits of miniaturisation in microelectronic devices? With respect to this question in 1986 the so called Size induced Metal-Insulator Transition (SIMIT) was defined by Nimtz et al. /4/. It expresses a decreasing conductivity when the

volume of metal particles is strongly reduced by fractionation, beginning with a diameter of 1  $\mu\text{m}$ , down to an experimental limit of below 20 nm. This effect was detected by dielectric measurements in the microwave range on small metal particles dispersed in oil. Its explanation claims that the conduction electrons form standing electron waves having discrete energies with multiples of the half of the de Broglie wavelength inside the metal particle leading to the picture of "particles in a box". The corresponding level splitting in the electronic states in this size regime is smaller than the characteristic thermal energy  $k_B T$ , so that the conductivity is only slightly affected by the temperature. The first attempt to take advantage of the SIMIT was the design of so-called Cut Off Wavelength (COW) - Transistors /4/. According to theory /5/ a more pronounced level splitting can be expected for smaller metal particles of few nanometers. For instance for gold particles with a diameter of 1 nm a

level splitting of approx. 100 meV might be expected /6/.

For the measurements described in the following the powdery sample material of Au<sub>55</sub> was condensed by pressing with a controlled high pressure. The pressed pellets of 5 mm in diameter and a thickness between 0.1 and 0.4 mm revealed a gravimetical defined density of more than 90 % of the theoretical closest sphere packing of this spherical molecules. Though re-dissolution in appropriate solvents, chemical and spectroscopic analysis an STM it was verified that the protecting ligand shells were not destroyed so that no noticeable aggregation could be detected.

The method of investigation was the Low Frequency Impedance Spectroscopy in a frequency range from 10 Hz to 10 MHz using the impedance analyzer HP 4192 A. 300 measurements in equidistant logarithmic steps in the constant voltage mode have been taken at various temperatures from ambient temperatures up to the respective limit of chemical stability from 253 to 333 K. During the measurements the discs were placed under protective gas between spring loaded parallel noble metal electrodes in a brass capacitor.

A very characteristic feature of all measurements is the appearance of two relaxation modes in the kHz and MHz range /6,7/. In contrast, if the clusters were embedded into non-polar polymers like polystyrene, they did not show either relaxation process. The two relaxation processes have been resolved by mathematical fitting using numerical approximations. Like it is shown in figure 2 the total response of the sample, which is here plotted as the real part of the impedance  $Z'$  against the imaginary part of the impedance  $Z''$  in the complex plane, can be described by the circuit equivalent shown above the experimental curve. Below the measured curve each separate semicircle is plotted belonging to the separate links. In each measurement one of the two elements is always an ideal Debye type and both semicircles can visually recognized only in the

total non-fitted spectra measured at the highest temperatures. From temperature dependant measurements the activation enthalpies were determined from an Arrhenius-behavior  $\sigma \sim (T/T_0)^{-1}$ , which is for the Au<sub>55</sub>-cluster 0.15 eV and 0.16 eV respectively for the two processes. Deviation from simply activated behavior could not be made in this high temperature range although former AC and DC measurements on this material /8/ revealed in a wide temperature range from 70 K up to the thermal limits of stability that  $\sigma_{DC} \sim (T/T_0)^{-1/2}$ . By applying different models of hopping conductivity to this data and including the AC behaviour and the field dependance of the conductivity, it was reported that the total conductivity can best be fitted with a thermally activated multiple site hopping process /8/.

According to this the Cole-Cole-process could be interpreted as an "inter-cluster" process due to the transport of electrons between neighboring clusters. This was supported by the fact that the Cole-Cole element could describe a distribution of relaxation times and hopping lengths respectively due to a slight disorder in the arrangement of the clusters. Further the exponent  $\alpha$  of this impedance function at 0.65 is a typical value for hopping conductivity, usually described by empirical power laws of the AC conductivity.

On the other hand the Debye process with a macroscopic relaxation  $\tau_{2macro}$  time of

$$\tau_{2macro} = R_2 \cdot C_2 \quad (1)$$

could be interpreted as an "intra-cluster" process, and is ascribed to ideal perfectly arranged cluster aggregates, in which the clusters are densest packed following the principles of closest packing /7/. This aggregates, which can be detected by a different analytical techniques, like X-ray diffraction /9/ - or STM-measurements /10/, consist mainly of 13 or 55 Au<sub>55</sub> clusters and are called clusters of clusters or "superclusters". Assuming that the standardized capacitance  $C_2$  of the Debye process

approximates the capacitance of these bulk regions with perfect cluster packing,  $C_2$  can be divided into the microscopic partial capacitances  $C_{micro}$  of single clusters /7/. This value lies, depending on the quality of package, in the range of  $1$  to  $5 \cdot 10^{-18}$  F. The normalized high temperature conductivity  $1/R_2$  for this process approximately fits the SIMIT-data /7/, which means that the metal clusters are still conducting but reveal a typical semiconducting behavior. Independantly the capacitance  $C_{micro}$  can also be calculated from the activation enthalpies by a macroscopic electrostatic approach basing on the assumption that the charging energy in a perfect arrangement of clusters is determined by the cluster size  $d$  and the inter-cluster distance  $s$ , which is the double thickness of the ligand shell (see figure 3). This also amounts  $C_{micro} \approx 10^{-18}$  F and gives a dielectric constant of  $\approx 4$  for the non conducting ligand shell. The value of  $10^{-18}$  F indicates that the charging energy  $E_c$  of a cluster in a perfect arrangement, which is given by

$$E_c = e^2 / 2C_{micro} \quad (2)$$

surmounts the thermal energy  $k_B T$  by more than a factor 6 at room temperature, allowing the establishment of a Coulomb barrier. This will be most likely proven by not yet completely evaluated STS-experiments on pressed cluster samples at Au<sub>55</sub> also at ambient temperature. The current-voltage characteristics verified the expected non-linear behavior for different distances between tip and sample with an appearance of a blockade region up to 0.9 V /6,10/.

In these densest arrangements, the electronic states of neighboring clusters are connected to each other in a way that in the ground states the electrons are localized in a still conducting cluster. These electrons are separated energetically from each other by the Coulomb energy for a transition of a single electron, which is called Single Electron Tunneling (SET)- process /11/.

In summary, by Impedance Spectroscopy it was shown that metal

clusters consisting of only 55 gold atoms are still conducting revealing the properties of a semiconductor. In arrangements of clusters the surrounding ligand shells act like a dielectric spacer between neighboring clusters and reveal capacitances down to  $10^{-18}$  F. At tunnel junctions with such small capacitances SET-processes are observable already at room temperature. These unique properties of ligand stabilized clusters and especially of cluster collectives make these materials very interesting for microelectronic devices basing on switching processes with single electrons /12/.

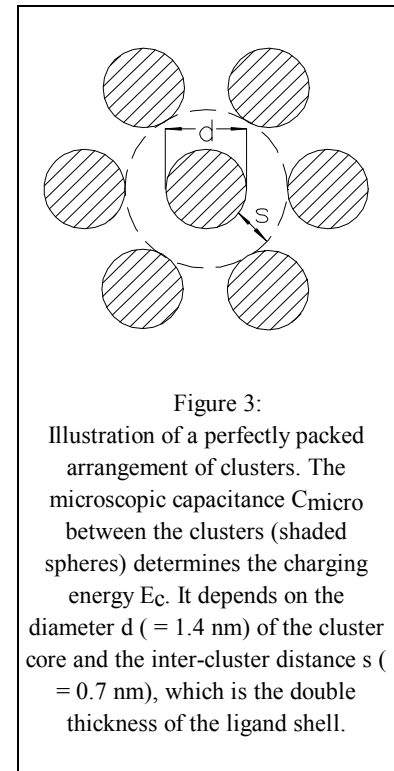


Figure 3:

Illustration of a perfectly packed arrangement of clusters. The microscopic capacitance  $C_{micro}$  between the clusters (shaded spheres) determines the charging energy  $E_c$ . It depends on the diameter  $d$  ( $= 1.4$  nm) of the cluster core and the inter-cluster distance  $s$  ( $= 0.7$  nm), which is the double thickness of the ligand shell.

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Dr. Ulrich Simon  
Institut für Anorganische Chemie  
Universität GH Essen  
Schützenbahn 70  
45127 Essen  
Germany

Prof. Dr. A. B. Szymanski

## The Dielectric and Related Phenomena Conference

The Dielectric and Related Phenomena Conference was held on 12-16 September 1994 at Zakopane - Koscielisko in Poland. It was the third in a series after conferences in Krynica /1992/. The main topics of the conference were : dielectric spectroscopy : theoretical background, experiment and application, charge transport in poorly conducting disordered media as well as high field phenomena. The conference was organized by the Department of Physics of the Technical University in Rzeszów, the organizer of the next, 1996 conference, the Technical University of Łódź in Bielsko - Biala and the private Cracow Institute of Technology with the participation of the organizer of the 1992 conference. The Steering Committee worked under Professor A.K. Jonscher. The Organizing Committee was headed by the undersigned.

The conference was held over five days (from the morning of the 12<sup>th</sup> until midday on the 16<sup>th</sup>) with a break in the middle, on Wednesday. The main lecturers presented gave talks on topics of a general nature (J. Janik, Molecular reorientation in liquid crystals via neutron scattering, dielectric relaxation and related methods; M. Kryszewski, Dielectric methods in interface studies ; G. Williams, Molecular dynamic and alignment behavior in liquid crystal polymers as studied by dielectric relaxation spectroscopy), on transport in amorphous materials (H. Bassler, Charge transport in random organic photoconductors, A. Bunde, M. Meyer, Anomalous transport in glasses), application of dielectric methods (D.K. DasGupta, Dielectric behavior of polyethylene), high voltage phenomena and breakdown (J.C. Fothergill, Recent advances in electrical degradation and breakdown in polymers R. Patsh, Advantages and problems of the use of polymers in high voltage applications) and theory

(K. Weron, Interconnection between the empirical and the theoretical "first passage" relaxation functions). The other contributions were in line with the overall field of the conference; the abstracts of the contributions are in "Conference Abstracts" (CIT, Cracow, Poland). There were also two panel discussions related to relaxation theory, and present and potential applications of dielectric methods.

The attendance at the conference was around sixty more than half being Polish.

The conference site, both accommodation and lecture halls, was located 7 km outside Zakopane, within walking distance of the Tatra Mountains National Park. Besides pleasant weather and trips to mountains the participants enjoyed a performance by folk artists during the conference banquet.

Among the sponsors of the conference were : Asea Brown Boveri Poland, the US Air Force, the Polish Ministry of National Education, Novocontrol GmbH, the Foundation of Science for Industry and the Environment.

Following the decision of the conference Steering Committees the next conference, DRP 96, will in the surroundings of Bielsko-Biala, Perhaps in a resort located in the Beskidy mountains. The Organizing Committee will be selected from the Bielsko-Biala Division of the Technical University of Łódź.

Those interested in this conference send for further information to : Prof. Dr A. Wlochowicz, Textile Institute, Technical University of Łódź, Division in Bielsko-Biala, 43-309 Bielsko-Biala, ul. Willowa 2, Poland

Prof. Dr. A. B. Szymanski  
Technical University  
Chair of Physics  
ul. W. Pola 2, 35-959 Rzeszów  
Poland

Prof. Jovan Mijovic

## Use of Impedance Spectroscopy to monitor progress of reactions in organic materials

### I. Introduction

A vigorous research activity has unravelled in recent years regarding fundamental and applied aspects of dielectric properties of polymeric materials. Fundamental dielectric investigations yield a wealth of information about molecular motions and relaxation processes, while a strong interest in the applied research reflects the growing use of polymers in batteries, fuel cells, coatings, encapsulants, electronic interconnect devices, printed board circuitry and microwave assemblies for radars. However, the extensive literature on dielectric behavior of polymers, accumulated in several books and key reviews (1-9), pertains almost exclusively to non-reactive systems. The application of impedance spectroscopy to monitor the **progress of reactions** in polymer-forming and non polymer-forming systems has a much more recent origin but has a great potential as a diagnostic tool for in-situ real time process control.

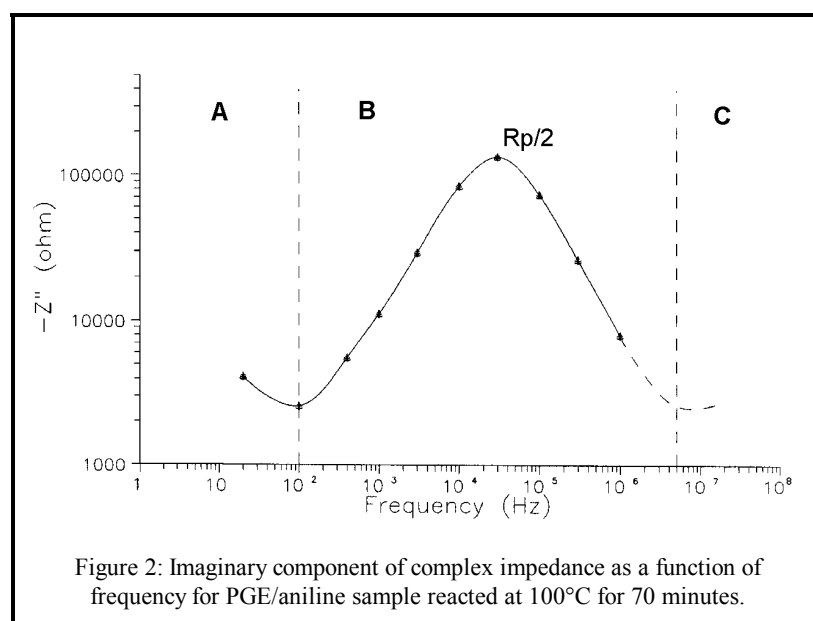
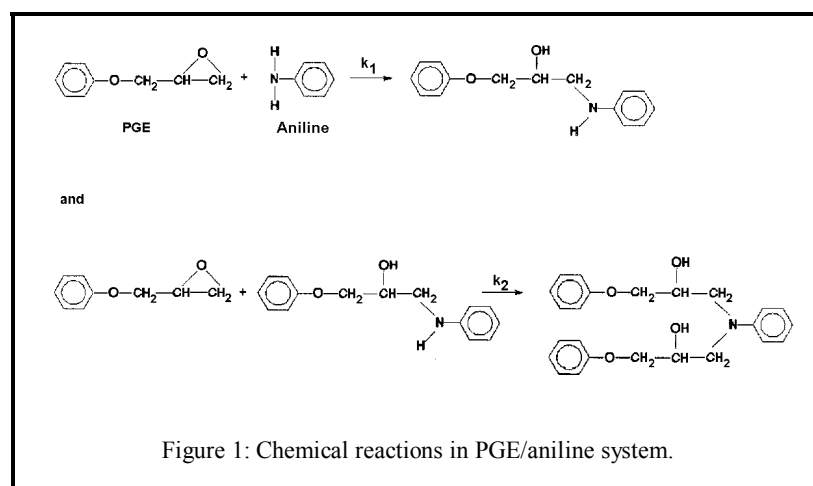
In this column I shall use some of our recent results to present an elegant methodology for analysis of dielectric properties of reactive organic systems by impedance spectroscopy.

### II. Experimental

The reactive mixture described here is a model system of a non polymer-forming type. It consists of 1,2-epoxy-3-phenoxypropane and aniline. The former compound is also known as phenyl glycidyl ether, or PGE. The reaction between PGE and aniline occurs in two consecutive steps shown in Figure 1. Results reported here were obtained with a stoichiometric mixture of aniline and PGE at a series of selected isothermal temperatures in the range between 90°C and 120°C.

Two pieces of equipment were used for dielectric measurements: 1) a Hewlett-Packard model 4284A Precision LCR Meter, operable in the frequency range from 20Hz to 1MHz; and 2) A Solartron 1260 Gain Phase Impedance Analyzer, operable in the frequency range from 10<sup>-6</sup>Hz to 32MHz. In the common frequency range, the two instruments could be used interchangeably without affecting the results. Novocontrol's BDS System, which is currently unavailable at Polytechnic, offers attractive possibilities for studies of dipolar relaxations owing to its upper frequency limit of 1GHz and. Our equipment was modified by the addition of a temperature-controlled chamber and was interfaced to peripherals via NI's IEEE 488.2 bus.

At each frequency, a low voltage AC excitation wave was applied to the metallic electrodes and the overall impedance measured. The excitation frequency was varied from the maximum of 10<sup>+6</sup>Hz to a minimum value that depended on the time and temperature of the measurement. Ten frequencies were swept in each measurement. For each reaction time, on average, five steps were taken at each of the ten frequencies. The time required to complete a frequency sweep depended on the lowest value of frequency ( $f_{\min}$ ) employed during the run. The time scale of the experiment was negligible in comparison with the time scale of the changes in the reactive system; hence each measurement could be taken to represent an isostructural state.



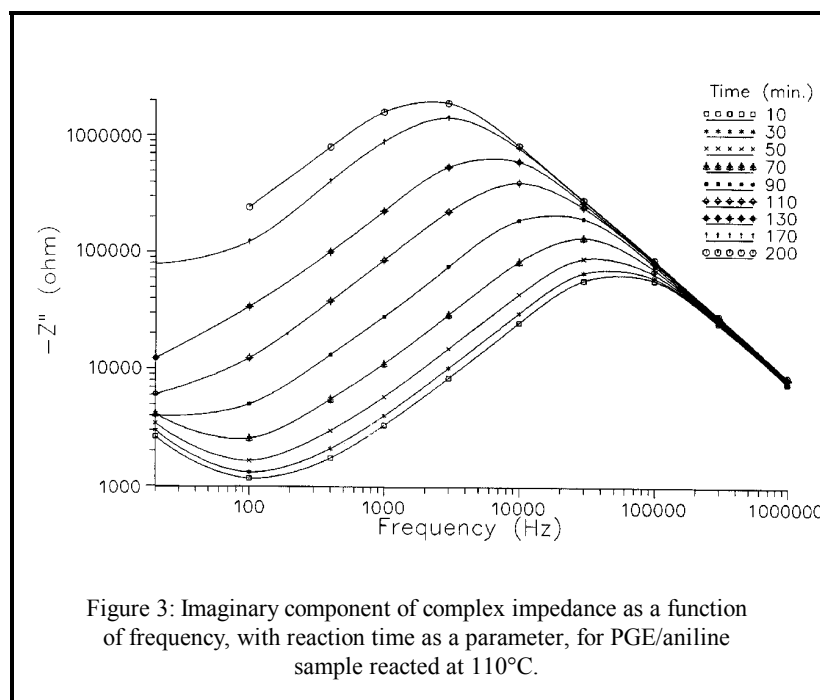


Figure 3: Imaginary component of complex impedance as a function of frequency, with reaction time as a parameter, for PGE/aniline sample reacted at 110°C.

The measuring cell consisted of two glass slides separated by a Teflon shim. Teflon was attached to glass on both sides using a special silicone adhesive transfer tape (Specialty Tapes' CW-14HT High Temperature Silicone Transfer Tape). Thin aluminum electrodes, with surface area of  $4\text{cm}^2$ , were placed on each glass plate. The cell constant,  $K=S/L$ , was equal to 25. Temperature was monitored with an embedded sensor adjacent to the measuring cell. The temperature inside the sample was verified in a series of calibration runs using Luxtron's Model 750 fluoroptic temperature probe. During tests, the cell was vertically held to allow for shrinkage without altering the distance between electrodes.

### III. Results

The models of dielectric behavior are based on series and/or parallel combinations of resistances (R) and capacitances (C) that can account for the contribution of all active mechanisms to the overall dielectric polarization. In-depth accounts of the fundamental aspects of equivalent circuit modelling are available in the literature (10-13), but, as a rule, they do not address the subject of **reactive** organic systems.

Resistance and capacitance of an equivalent circuit have the following physical meaning in our case. Migration of extrinsic and/or intrinsic charges is a dissipative process (it contributes to the dielectric loss but not to the dielectric permittivity) and is represented by resistance. Capacitance, on the other hand, measures the overall ability of our dielectric material to store the electric field. A single resistance that encompasses the dissipative contribution of all migrating charges, extrinsic and/or intrinsic alike, is sufficient here, since the dissipative contributions due to electrode polarization and dipolar relaxations fall outside the frequency range utilized in our analysis. Thus an R-C parallel circuit, its simplicity notwithstanding, represents an adequate phenomenological model of the dielectric response of our system at the frequencies investigated in this study.

By expressing complex impedance in terms of its real and imaginary components we obtain:

$$Z' = \frac{R}{1 + \omega^2 C^2 R^2} \quad (1a)$$

$$Z'' = \frac{\omega CR^2}{1 + \omega^2 C^2 R^2} \quad (1b)$$

Quantitative evaluation of the circuit parameters is based on the plots of imaginary impedance ( $Z''$ ) as a function of frequency. An example of such plot for PGE/aniline system at  $100^\circ\text{C}$  after 70 minutes of reaction, is shown in Figure 2. Three zones, roughly partitioned by frequencies  $f_1$  and  $f_2$ , are readily distinguishable in Figure 2: zone A - where electrode polarization dominates the dielectric response; zone B - which is of interest here and where dissipative effects caused by charge migrations play the major role; and zone C - where contributions from dipolar relaxations prevail. But in zone B, the dielectric signal is not affected by either electrode polarization or dipolar relaxations and, in that frequency range, we can utilize a R-C parallel circuit, whose imaginary impedance is described by equation 1b. Taking a derivative of  $Z''$  with respect to angular frequency we get:

$$\frac{dZ''}{d\omega} = \frac{CRp^2(1 - \omega^2 R p^2 C^2)}{(1 + \omega^2 R p^2 C^2)^2} \quad (2)$$

Equation 2 is equal to zero when:

$$Z''_{\max} = \frac{R_p}{2} \quad (3)$$

and thus the unknown resistance R is obtained directly from  $Z''_{\max}$ . An apparent conductivity ( $\sigma$ ) and/or resistivity( $\rho$ ) due to migrating charges, can be calculated from the following equation:

$$\sigma = \frac{1}{\rho} = \frac{L}{RS} \quad (4)$$

where  $S/L$  denotes the cell constant.

Let us now revert our attention to the changes in complex impedance **during reactions**. Since each frequency sweep, as established earlier, involves an isostructural state, we conducted impedance measurements at selected time intervals during reaction. The variation in impedance during reaction was systematic, extremely reproducible and reliable. In Figure 3 we show a

plot of imaginary impedance as a function of frequency, with reaction time as a parameter, for isothermal run at 110°C. Various interesting observations were made, but most importantly, values of  $Z''$  in zone B are dominated solely by the dissipative contribution of migrating charges. The value of resistance calculated from equation 4 is therefore a true measure of the dissipative character of migrating charges. Our results clearly stress the necessity of data collection over a wide frequency range if one were to distinguish between different polarization mechanisms, a practice all too often overlooked in the literature.

Utilizing data of the type shown in Figures 3 and equation 4, we can calculate resistivity due to migrating charges at any time and temperature in the course of reaction. In Figure 4, we show the calculated resistivity as a function of time for PGE/aniline reactions at 90, 100, 110 and 120°C. During reaction, an S-shaped curve was observed at each temperature, characterized by an initial increase in resistivity and a subsequent levelling off to an asymptotic value. The resulting behavior bears a qualitative resemblance to the trend displayed by extent of reaction. This analogy has been noted and exploited in empirical fashion by several researchers (e.g.14

and references therein). In this study, we have selected an equation based on the early work by Keinle and Race (15) and later successfully utilized by Nass and Seferis (16), which is of the following general form:

$$\alpha/\alpha_m = (\log p - \log p_0)/(\log p_m - \log p_0) \quad (5)$$

where  $\alpha_m$  denotes the maximum (limiting) extent of reaction due to vitrification in polymer networks (17). Equation 5 was then used to calculate the extent of reaction from impedance data. The results for PGE/aniline reaction at 100, 110 and 120°C are shown in Figure 5. The extent of reaction was also calculated from High Performance Liquid Chromatography (HPLC) data (18) and plotted together with the dielectric value in Figure 5. The observed agreement between the results generated by the two techniques is remarkable!

In conclusion, complex impedance is a versatile real time diagnostic tool which varies systematically during reaction, is extremely reproducible and reliable, can be applied to virtually any reactive system, resembles qualitatively the corresponding chemorheological changes, and is conducive to the development of models based on equivalent circuitry. Nonetheless, a realization of its full potential necessitates that fundamental correlations be developed between the dielectric response and the chemorheological changes in reactive systems.

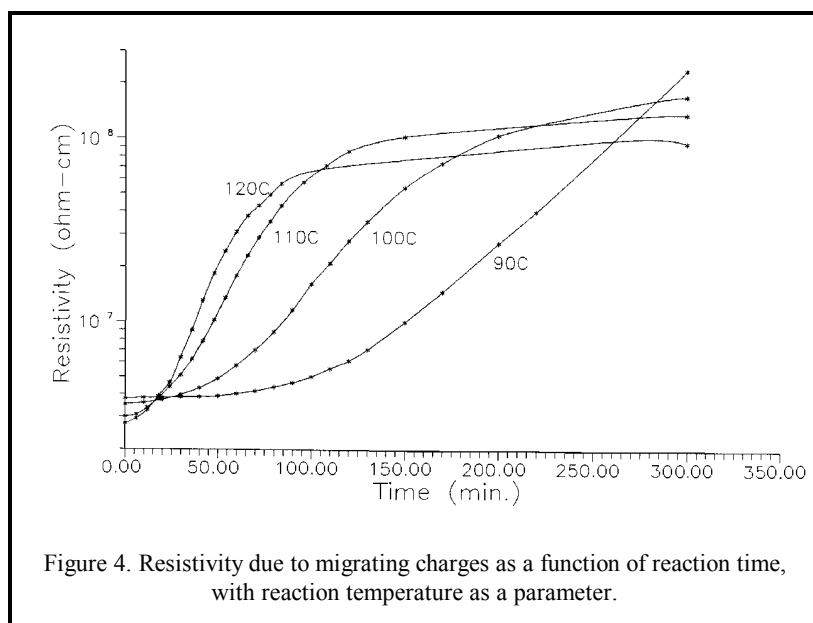


Figure 4. Resistivity due to migrating charges as a function of reaction time, with reaction temperature as a parameter.

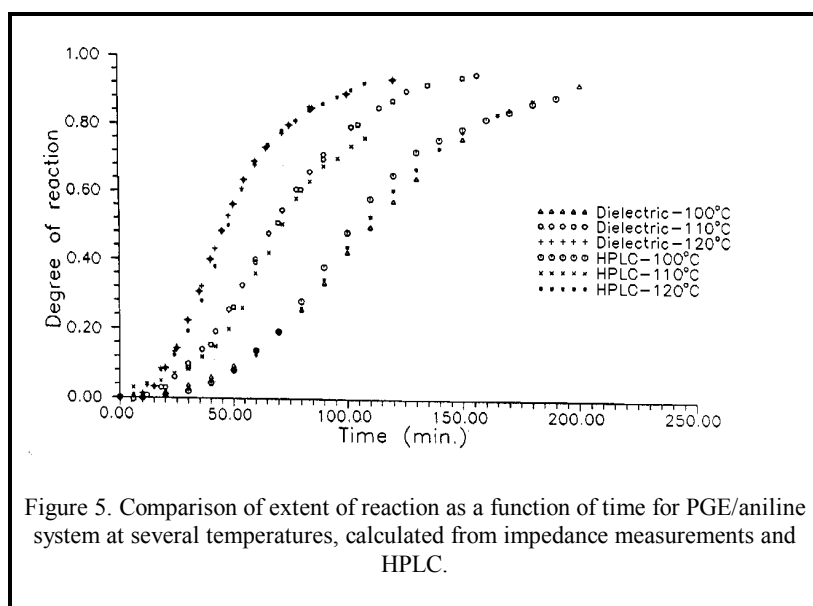


Figure 5. Comparison of extent of reaction as a function of time for PGE/aniline system at several temperatures, calculated from impedance measurements and HPLC.

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Prof. Jovan Mijovic  
 Professor of Chemical Engineering  
 Polytechnic University  
 Six MetroTech Center  
 Brooklyn, NY 11201 USA

Dr. Yuri Feldman

## New Time Domain Dielectric Spectrometer

The time domain technique involves the application of a rectangular step-voltage pulse to the sample and the monitoring of the changes in the characteristics of the pulse after the reflection from a section of a co-axial line filled with the sample being tested. Time-domain methods facilitate high-frequency measurements over the traditional network analyzer approach. In the time-domain method, the response of the sample to a fast voltage transient is captured in the time domain and converted to complex frequency response using a Fourier-Laplace transform. Measurements are made along a coaxial transmission line with the sample mounted in a capacitive sample cell that terminates the line. The only differences between different set-ups are in the construction of the measuring cell and its location in the coaxial line, which lead to different relationships between the values registered during the measurement and the dielectric characteristics of the objects under study. The limiting high and low frequencies are determined by the rise time and duration of the

step pulse.

In the real system, the test signal applied to the sample contains in itself the transfer function of the sampler and of the whole coaxial line. In order to exclude the incident pulse convoluted with the "parasite" set-up function in calculations of the dielectric parameters one can use the total difference method. The general idea of the method is to measure only the signals from the sample holder with two known samples and one sample being tested.

Fig. 1 presents a block-diagram of the set-up. It consists of the Dipole TDS LTD time domain measuring system with a two-channel (A and B) sampler, a step generator, a thermostabilised sampling head, a digital acquisition system (DAS), and a computer, PC AT 486/66. The construction of thermostabilized sample holders with gold electrodes is based on the principle of "lumped capacitance" and required a quite small amount of the sample being tested (less than 5 mg for solid sate materials or less than 200  $\mu$ l for liquid samples). The use of a soft-touch sample cell is also possible. The temperature can be computer-controlled in our setup over the interval of  $-30 \div +120^{\circ}\text{C}$ . The system utilizes the difference method of

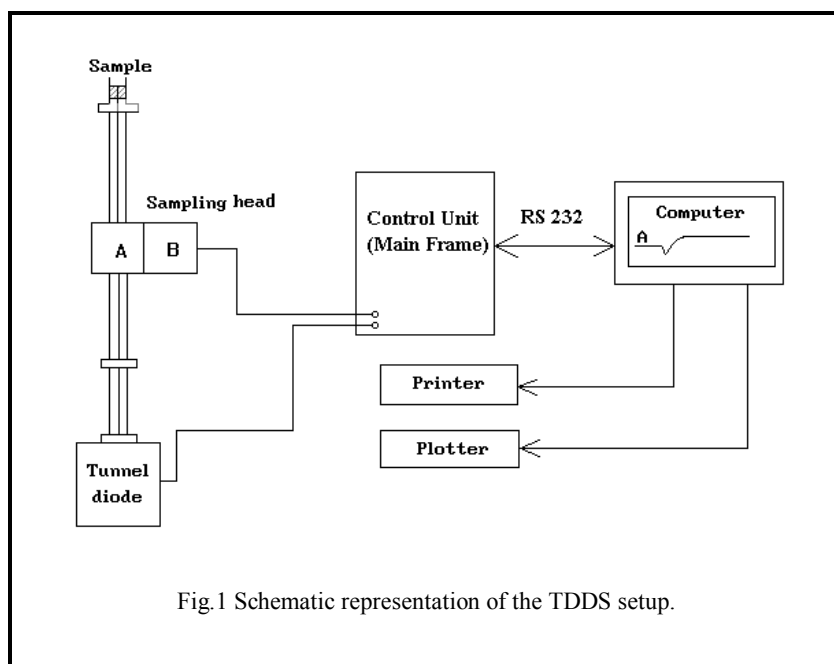


Fig.1 Schematic representation of the TDDS setup.



measurement, with a unique registration of primary signals in a non-uniform time scale. This system permits five orders of frequency ( $10^5$ - $10^{10}$  Hz) to overlap in one single measurement. The results can be presented both in frequency (in terms of complex dielectric permittivity  $\epsilon^*(\omega)$ ) and in time (in terms of the dielectric response function  $\phi(t)$ ) domains.

Time Domain Dielectric Spectroscopy now makes it possible to investigate the Dielectric relaxation processes in a wide range of systems (Biological, Physiological, Chemical, Material Science), be they liquids, solids or films.

Dr. Yuri Feldman, Ass. Prof. of the School of Applied Science The Hebrew University of Jerusalem Givat Ram, Casali Bldg. Jerusalem 91904, Israel

Dr. Gerhard Schaumburg

## Data Evaluation and Measurement Control Software for Dielectric Research

In modern measurement systems, the system performance is mainly depending on the quality of the software. For dielectric measurements, some general software packages are dealing with several special aspect. For example there are programs controlling several analyzers or temperature control systems. Other programs perform data evaluation or presentation. Data fitting is possible by using general mathematical software. In most cases data formats of different applications are incompatible, so that researchers have to develop conversion programs or

in the userfriendly MS-Windows environment.

WinDETA performs the measurement control, basic data evaluation and data representation. It supports ten of the most well-known impedance analyzers for dielectric measurements and three temperature control systems. All devices are controlled by an unique user interface, while technical details are hidden in the software. The user simply selects an actual device configuration, while all other options of WinDETA like data evaluation, measurement control and data representation remain unchanged. The advantage of this concept is, that even measurements with different device combinations are performed in standardized and documented fashion. Therefore, the results can be easier compared and the probability for performing invalid measurements decreases. Last not

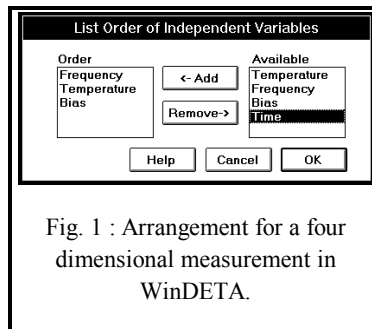


Fig. 1 : Arrangement for a four dimensional measurement in WinDETA.

even complete programs themselves. The procedure from starting the first measurement to the final plot involves a lot of time consuming steps with little chances to automate these. Moreover, the complete procedure is seldom documented and new researchers find it difficult to operate.

In order to improve this situation, NOVOCONTROL has developed a software package specialized on dielectric analysis. The concept was to create software handling dielectric measurements and their evaluation with a high amount of standardization and automatization. The NOVOCONTROL software has been developed in close co-operation with researchers active in dielectric analysis and therefore contains nearly all features of practical importance. NOVOCONTROL offers the programs WinDETA and WinFIT both working

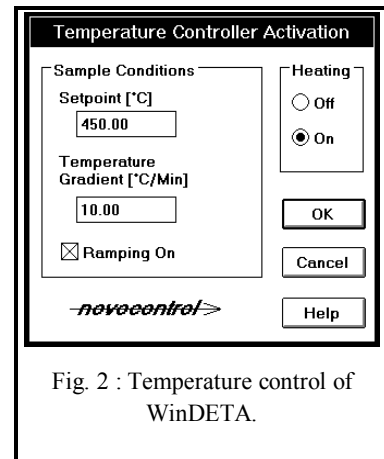


Fig. 2 : Temperature control of WinDETA.

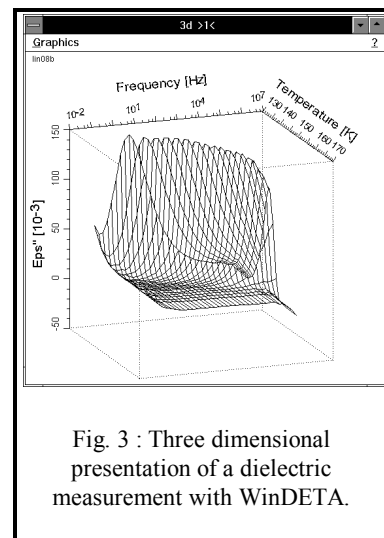


Fig. 3 : Three dimensional presentation of a dielectric measurement with WinDETA.

least, performing measurements with various devices becomes very easy.

WinDETA supports value lists for the independent quantities frequency, temperature, time and dc-bias, which may be arranged in arbitrary order up

representations (fig. 3). Data are exported to other applications as high resolution graphics or as ASCII tables.

In addition to 2D- and 3D- presentations, WinFIT performs analytic evaluations of the dielectric

$$\epsilon^*(\omega) = \epsilon' - i\epsilon'' = -i \left( \frac{\sigma_0}{\epsilon_0 \omega} \right)^N + \sum_{k=1}^3 \left[ \frac{\Delta \epsilon_k}{(1 + (i\omega\tau_k)^{\alpha_k})^{\beta_k}} + \epsilon_{\infty k} \right]$$

Fig. 4

to measurements with five dimensions. An example of a four dimensional set up is shown in fig. 1.

In this configuration WinDETA is performing a three dimensional frequency - temperature dependent measurement for each point of the dc-bias list.

Temperature control is performed either automatically as a part of WinDETA's measurement control or manually. Heating or cooling rates may be specified. Therefore the speed of the temperature change between two points can be defined (fig. 2).

From the measured impedance all dielectric quantities like the dielectric function, conductivity and so on are evaluated. These data are displayed in several two- or three dimensional

spectra  $\epsilon = \epsilon' - i\epsilon''$ .

The measured data can be interactive graphically manipulated. This includes shifting, deletion and insertion of data points with the mouse, multiplication of data curves and connection of data curves being measured in different frequency ranges.

The main feature of WinFIT is non linear curve fitting of the measured data in the frequency domain. The fit function is a Havriliak Negami Function  $1/$  (fig. 4) with up to three terms and a conductivity term, where  $\omega = 2\pi$  frequency and  $\epsilon_0$  denotes the vacuum permittivity.

Figure 6 shows the real and imaginary part  $\epsilon'$  and  $\epsilon''$  of the fit function with a conductivity term and

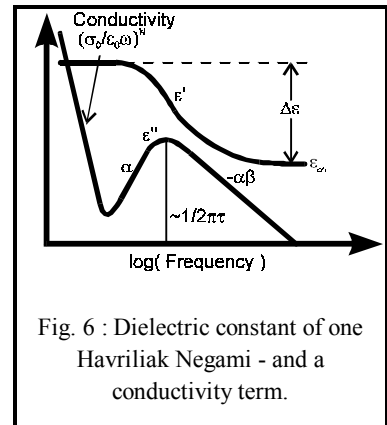


Fig. 6 : Dielectric constant of one Havriliak Negami - and a conductivity term.

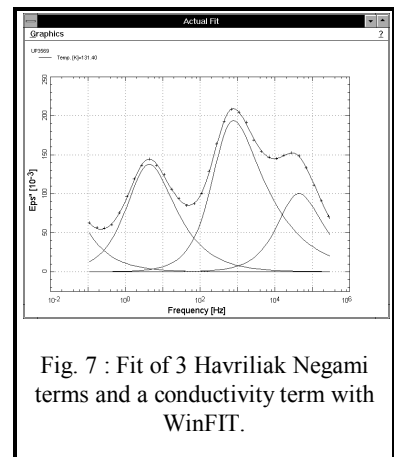


Fig. 7 : Fit of 3 Havriliak Negami terms and a conductivity term with WinFIT.

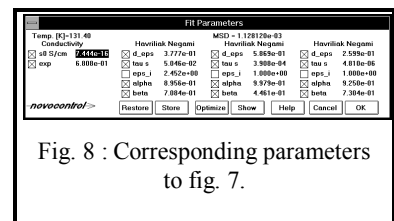


Fig. 8 : Corresponding parameters to fig. 7.

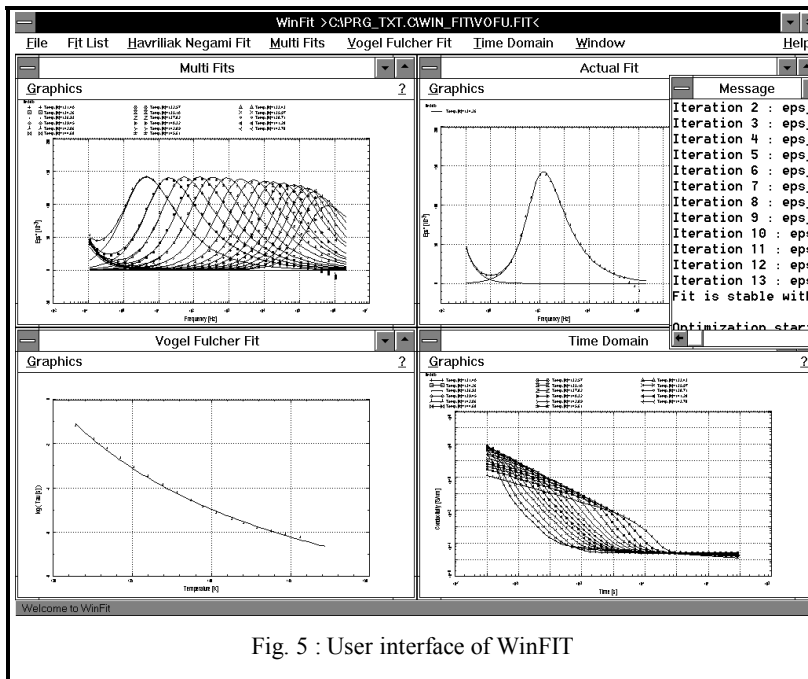


Fig. 5 : User interface of WinFIT

one Havriliak Negami term. The increase at low frequencies in  $\epsilon''$  is due to the conductivity term. The slope of the increase is determined by the exponential factor  $N$  which in most cases is equal to 1.

The Havriliak Negami term shows a dielectric relaxation.  $\Delta\epsilon$  is the difference in  $\epsilon'$  at very low and infinite frequencies.  $\Delta\epsilon$  is also proportional to the area below the  $\epsilon''$  relaxation peak.

The value of  $\epsilon'$  at infinite frequencies is determined by  $\epsilon_{\infty}$ .  $\tau$  specifies the relaxation time. The width parameter  $\alpha$  specifies the slope of the low frequency side of the relaxation in  $\epsilon''$ .

$\beta$  is the asymmetry parameter.  $-\alpha\beta$  gives the slope of the high frequency side of the relaxation in  $\epsilon''$ .

The Havriliak-Negami equation includes the equations of Debye, Cole-Cole /3/ and Cole-Davidson /4, 5/. These functions can be fitted to the data in terms of the dielectric constant  $\epsilon'$ ,  $\epsilon''$ , the conductivity  $\sigma'$ ,  $\sigma''$ , the impedance  $Z'$ ,  $Z''$ , the capacity C, the resistance R and the loss factor  $\tan(\delta)$ .

As WinFIT was specially designed for Havriliak-Negami fits, the performance is very high. A fit to a

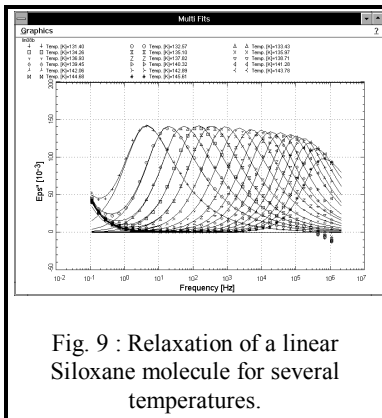


Fig. 9 : Relaxation of a linear Siloxane molecule for several temperatures.

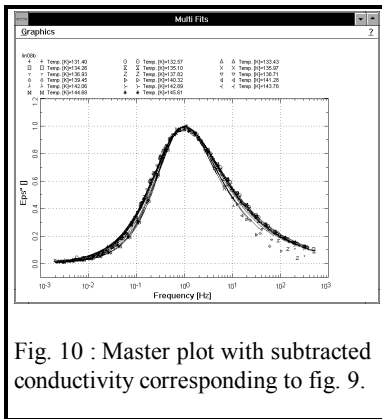


Fig. 10 : Master plot with subtracted conductivity corresponding to fig. 9.

curve with 50 data points on a 486 PC with 33 MHz is performed in less than 10 seconds. After completed a fit, WinFIT offers an option to subtract the conductivity term of the fit function from the measured data. This allows to display measured spectra without the conductivity contribution.

Generally a series of frequency sweeps at different temperatures or other independent variables like time and dc-bias is performed. For this reason, WinFIT allows to load a series of measurements in the frequency domain. These spectra series can be

fitted automatically without an interaction of the user. All data are simultaneously displayed in a multi graphics window together with the fit functions and their single terms.

WinFIT also offers a Master Plot option, which scales all the spectra in the multi graphics window in such a way, that the maximum in  $\epsilon''$  is located at 1 on the y-axis and at frequency of 1 Hz at the x-axis. The user can switch between the normal scaling and the master scaling. Also the option of subtracting conductivity can be used in the master plot representation.

If a fit series is complete, the Vogel-Fulcher window can be opened. This window shows an activation plot of the fit series in which the time constants  $\tau$  of each Havriliak Negami term against  $1/\text{temperature}$  are displayed. In addition, the Vogel-Fulcher function /6/ which corresponds to the Williams Landel Ferry (WLF) law is displayed and also may be fitted to the data. Instead of the time constants  $\tau$ , also the values  $\tau_{\text{max}}$  can be fitted and displayed, where  $\tau_{\text{max}}$  is the reciprocal value of the function.

As a further feature, WinFIT can transform the fit functions from the frequency domain into the time domain. This is done by calculating the Debye relaxation time distribution  $G(\tau)$  for all Havriliak Negami terms of the fit function.  $G(\tau)$  is defined as :

$$\epsilon^*(\omega) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty) \int_0^\infty \frac{G(\tau)}{1 + i\omega\tau} d\tau \quad (1)$$

where  $\epsilon^*(\omega)$  is the fitted frequency dependent dielectric function, and  $\epsilon_\infty$ ,  $\epsilon_s$  are the dielectric constant at infinite and zero frequency.

For a superposition of Havriliak Negami Terms,  $G(\tau)$  is available as an analytic expression /2/. The transformation to the time domain is done by using the step answer function /e.g. 7/

$$\psi(t) = 1 - \int_0^\infty G(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau \quad (2)$$

describing the polarization response to a constant electric field switched on

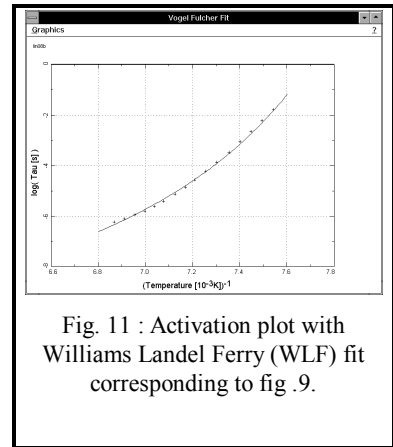


Fig. 11 : Activation plot with Williams Landel Ferry (WLF) fit corresponding to fig. 9.

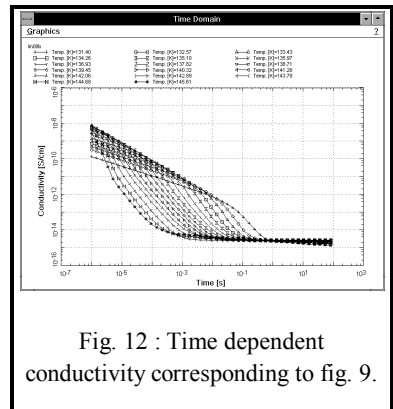


Fig. 12 : Time dependent conductivity corresponding to fig. 9.

at  $t = 0s$ . (2) is connected to the peak response by

$$\Phi(t) = \frac{d}{dt} \psi(t) \quad (3)$$

From (2) and (3), the time dependent dielectric constant and conductivity are calculated by

$$\epsilon(t) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty) \psi(t) \quad (4)$$

and

$$\sigma(t) = \sigma_0 + \epsilon_0(\epsilon_s - \epsilon_\infty) \Phi(t) \quad (5)$$

where  $\sigma_0$  denotes the dc-conductivity. WinFIT calculates all quantities defined in (1) - (5). An example for the time dependent conductivity is shown in fig. 12.

WinFIT supports various file formats. The data are imported either from NOVOCONTROL WinDETA or DETA for DOS result files or in flexible ASCII format, which can be configured by the user. A complete series of fits including data, fit functions and the Vogel-Fulcher fit can be saved and reloaded in one file with binary format. WinFIT exports

the following data as ASCII files, in order to be used in other applications :

- An ASCII table with the parameters of each term of the fit function in dependence of temperature, time or dc-bias.

- A series of files with measured data, manipulated by the subtract conductivity and master plot options or by user with the data editing options.

- A series of files with the fit functions as separate points. The subtract conductivity and master plot

options are stored also.

- A series of files with the fit functions in the time domain as separate points.

- Finally, all configurations of WinFIT including the window placement can be saved and reloaded in preset files.

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Dr. Gerhard Schaumburg,

NOVOCONTROL GmbH

Obererbacher Str. 9, 56414 Hundsangen,

Germany

Dielectrics Newsletter is published by: NOVOCONTROL GmbH  
Obererbacher Str. 9  
56414 Hundsangen  
Germany



fax:

Email:

Editors:

++49 - 6435 - 96230

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100257.263@compuserve.com

Dr. Gerhard Schaumburg

Robert den Dulk

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