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Complex polarizability as used to analyze dielectric relaxation measurements

E. Sánchez Martínez, R. Díaz Calleja, and W. Gunßer[1])

Laboratory of Thermodynamics and Physical Chemistry of E.T.S.I.I.V. Valencia (U.P.V.), Spain, and
[1]) Institute of Physical Chemistry, University of Hamburg, FRG

Abstract: The effect of representing dielectric properties in terms of the complex polarizability $\alpha^* = \alpha' - i\alpha''$ is examined. Loss curves (ε'' and $\tan\delta_\varepsilon$) are shifted towards higher frequencies, revealing the existence of new relaxations and allowing the clarifications of ones already known. We have calculated the shift ratios ω (at maximum α'' or $\tan\delta_\alpha$)/ω (at maximum ε'' or $\tan\delta_\varepsilon$) from the more conventional empirical equations representing the dielectric behavior. Some examples are given.

Key words: Polarizability; dielectric relaxation; charge transfer complexes; polymers

Introduction

Several years ago, Scaife [1] proposed a method for analyzing the dielectric response in which the dielectric permittivity ε^* could be replaced by polarizability α^* defined as

$$\alpha^* = \frac{\varepsilon^* - 1}{\varepsilon^* + 2}$$
$$\alpha^* = \alpha' - i\alpha'' \,. \qquad (1)$$

This is justified if the long-range dipole-dipole coupling vanishes in a spherical cavity containing dielectric material. The arguments of Scaife are essentially macroscopic and are therefore free of any molecular details. Scaife pointed out that the reaction field responsible for Kirkwood's theory [2] will be out of phase in a dynamic sinusoidal alternating field and, because of this, the special effects concerning this reaction field observed at equilibrium will not be observed. Polarizability α^*, as given by Eq. (1), is also related to a macroscopic (although intrinsic) relaxation time.

On the other hand, complex polarizability is not a new concept. It has been, for example, introduced by Böttcher et al. [3] in a similar context as the best way for characterizing the pulse-response function of a spherical dielectric specimen.

Moreover, in a classical paper by Havriliak and Negami [4] the polarizability α^* is introduced via the approach of R. H. Cole [5], who consider the time-dependent correlation of electric moment of the sample including all the moments (permanent and induced) giving

$$\frac{\varepsilon^* - 1}{\varepsilon^* + 2} = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} + 4\pi N \frac{\langle \mu(0) \cdot M(0) f^0 \rangle}{9kTV} \times L(-\dot{\psi}(t)) \,, \qquad (2)$$

where

$$\psi(t) = \frac{\langle \mu(0) \cdot M(t) f^0 \rangle}{\langle \mu(0) \cdot M(0) f^0 \rangle}$$

is the decay correlation function, $\mu(0)$ the microscopic dipolar moment, and $M(t)$ the sum of the permanent moments in the macroscopic sphere. L is the Laplace transform, and the dot $(\cdot)$ indicates time derivation.

Formula (2) is in fact, a generalization of the classical Debye formula [6], in which $(\varepsilon - 1)M/(\varepsilon + 2)\rho$ is the molar polarizability. The term

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{4\pi N}{3V}\alpha \tag{3}$$

is the instantaneous polarization of the sphere according to Clausius-Mossotti [7], including the atomic and electronic, i.e., elastic polarization. $(\varepsilon^* - 1)/(\varepsilon^* + 2)$ is the polarization of the macroscopic sphere under consideration, and α^* the macroscopic polarizability.

Polarizability has been successfully applied to powdered donor-acceptor complexes (chalcogenides/TCNQ) by one of us (Sánchez Martínez) [8], revealing clearly the relaxation mechanism in the substances. It has also been used for a zeolite [9].

Interest in using the polarizability α^* as defined by Eq. (1) as opposed to permittivity in analyzing dielectric properties in materials is founded upon the following considerations:

1) As pointed out by Havriliak and Negami [4], for the purpose of comparison between dielectric and mechanical dispersions, it is more convenient to use the polarizability α^* than the permittivity ε^* as the dielectric property in connection with the displacement δ^* (defined from J^*, the dynamic compliance, in a similar manner as α^* is from ε^*).
2) Polarizability more clearly accentuates the high frequency zones of a relaxation, revealing in some cases new relaxation mechanisms.
3) The use of polarizability reveals relaxation peaks and allows subsequent calculation of apparent activation energies.
4) Finally, it provides a means for comparing dielectric behavior of substances with widely differing values of ε_0 since α' lies in the range between 0 and 1, whereas ε' (and ε_0) can differ significantly from unity.

The purpose of this paper is to examine in detail the transformation given by (1) and to test its validity for analyzing characteristic relaxation time shifts (or corresponding frequencies) of α^* with respect to ε^*. Using customary semiempirical equations, we have obtained quantitative estimates of the shifts in the frequency axis from the ε'' to the α'' loss peaks. To obtain reliable conclusions, it is necessary to discuss the shape of the ε'' vs ε' Cole–Cole plots in comparison to similar α'' vs α' plots with reference to the parameters appearing in the semi-empirical adjusted equations. Some applications are discussed.

Formal background and empirical equations

From (1), we can easily obtain the real and imaginary parts of α^*:

$$\alpha' = \frac{(\varepsilon' - 1)(\varepsilon' + 2) + \varepsilon''^2}{(\varepsilon' + 2)^2 + \varepsilon''^2}, \tag{4}$$

$$\alpha'' = \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2}. \tag{5}$$

By analogy to the loss permittivity, we can define a "loss tangent polarizability" as

$$\tan\delta_\alpha = \frac{3\varepsilon''}{(\varepsilon' - 1)(\varepsilon + 2) + \varepsilon''^2}. \tag{6}$$

This loss tangent polarizability can be understood as an intrinsic loss in the material.

Now, we will examine several empirical or semi-empirical equations representing the dielectric behavior of materials.

a) Debye semicircular arc: [10]
If we use the Debye equation

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau_\varepsilon} \tag{7}$$

in connection with (2), we obtain

$$\alpha' = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} + \frac{\dfrac{\varepsilon_0 - 1}{\varepsilon_\infty + 2} - \dfrac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}}{1 + \left(\dfrac{\varepsilon_\infty + 2}{\varepsilon_0 + 2}\right)^2 \omega^2\tau_\varepsilon^2}, \tag{8a}$$

and

$$\alpha'' = \frac{\dfrac{3(\varepsilon_0 - \varepsilon_\infty)}{(\varepsilon_0 + 2)^2}\omega\tau_\varepsilon}{1 + \left(\dfrac{\varepsilon_\infty + 2}{\varepsilon_0 + 2}\right)^2 \omega^2\tau_\varepsilon^2} = \frac{\dfrac{3(\varepsilon_0 - \varepsilon_\infty)}{(\varepsilon_0 + 2)(\varepsilon_\infty + 2)}\cdot\left(\dfrac{\varepsilon_\infty + 2}{\varepsilon_0 + 2}\right)\omega\tau_\varepsilon}{1 + \left(\dfrac{\varepsilon_\infty + 2}{\varepsilon_0 + 2}\right)^2 \omega^2\tau_\varepsilon^2}. \tag{8b}$$

From these equations we define:

– relaxed polarizability:

$$\alpha_0 = \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}; \tag{9a}$$

– unrelaxed polarizability:

$$\alpha_\infty = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\,; \tag{9b}$$

– "intrinsic relaxation time":

$$\tau_\alpha = \tau_\varepsilon \frac{\varepsilon_\infty + 2}{\varepsilon_0 + 2}\,. \tag{9c}$$

We also obtain:

$$\varepsilon_0 = \frac{2\alpha_0 + 1}{1 - \alpha_0}\,, \quad \varepsilon_\infty = \frac{2\alpha_\infty + 1}{1 - \alpha_\infty}\,,$$

$$\tau_\varepsilon = \tau_\alpha \frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2}\,, \quad \tau_\alpha = \frac{1 - \alpha_\infty}{1 - \alpha_0}\,. \tag{10}$$

Equations (8a, b) become:

$$\alpha' = \alpha_\infty + \frac{\alpha_0 - \alpha_\infty}{1 + \omega^2\tau_\alpha^2}\,, \quad \alpha'' = \frac{(\alpha_0 - \alpha_\infty)}{1 + \omega^2\tau_\alpha^2}\,\omega\tau_\alpha\,. \tag{11}$$

It is well known [3] that ε'' (and a fortiori α'') attains a maximum at $\omega_\varepsilon = \tau_\varepsilon^{-1}$ ($\omega_\alpha = \tau_\alpha^{-1}$ for α''). This fact implies that a maximum in an ε'' plot for a Debye material at ω_ε corresponds to a maximum in α'' at a frequency

$$\omega_\alpha = \omega_\varepsilon \frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2}\,. \tag{12}$$

Obviously, $\omega_\alpha > \omega_\varepsilon$, implying that the maximum shifts to higher frequencies as the separation between ε_0 and ε_∞ increases. This result can also be obtained by derivation of α'' with respect to ω in (8b) and by subsequent substitution of the real and imaginary parts of ε^*. By an identical procedure, we obtain from $\tan\delta$ a maximum at

$$\omega'_\alpha = \omega_\varepsilon \left\{ \frac{(\varepsilon_0 - 1)(\varepsilon_0 + 2)}{(\varepsilon_\infty - 1)(\varepsilon_\infty + 2)} \right\}^{1/2}\,. \tag{13}$$

Since ω_ε refers to the frequency at the maximum of ε'', we can relate this value to ω'_ε (the frequency at which $\tan\delta_\varepsilon$ attains a maximum) as follows:

$$\omega'_\varepsilon = \omega_\varepsilon \left(\frac{\varepsilon_0}{\varepsilon_\infty} \right)^{1/2}\,. \tag{14}$$

By combining (13) and (14), we obtain:

$$\omega'_\alpha = \omega'_\varepsilon \left\{ \frac{\varepsilon_\infty(\varepsilon_0 - 1)(\varepsilon_0 + 2)}{\varepsilon_0(\varepsilon_\infty - 1)(\varepsilon_\infty + 2)} \right\}^{1/2}\,.$$

Figure 1 gives an account of each of these four values in a generic example.

However, few substances follow a Debye behavior.

b) Cole–Cole equation: [11]

Many substances have a distribution of relaxation times that can be expressed in some cases as a modified Debye equation in the form of a Cole–Cole equation:

$$\varepsilon^* = \varepsilon' - \mathrm{i}\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (\mathrm{i}\omega\tau_\varepsilon)^{1-h}}$$

$$\text{with } 0 < 1 - h < 1\,. \tag{15}$$

This is a realistic model for the relaxations of many organic substances and small molecular groups in polymers. Substitution of the real and imaginary parts of (15) into (5) gives, after equating the derivative of α'' with respect to ω to zero and following some tedious algebra:

$$\omega_\alpha = \omega_\varepsilon \left(\frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2} \right)^{\frac{1}{1-h}}\,. \tag{16}$$

In the same manner, we obtain for ω'_α (maximum for $\tan\delta_\alpha$)

$$\omega'_\alpha = \omega'_\varepsilon \left\{ \frac{\varepsilon_\infty(\varepsilon_0 - 1)(\varepsilon_0 + 2)}{\varepsilon_0(\varepsilon_\infty - 1)(\varepsilon_\infty + 2)} \right\}^{\frac{1}{2(1-h)}}\,, \tag{17}$$

where

$$\omega'_\varepsilon = \omega_\varepsilon \left(\frac{\varepsilon_0}{\varepsilon_\infty} \right)^{\frac{1}{2(1-h)}}\,. \tag{18}$$

In the derivation of (16) and (17) we have used the equality of the parameter h in the ε and α representations of the dielectric data. In fact, it is easy to prove that by the $\varepsilon^* \to \alpha^*$ transformation h does not very.

Substitution of ε' and ε'' from (15) in (5) yields after rearrangement:

$$\alpha'' = \frac{3(\varepsilon_0 - \varepsilon_\infty)(\omega\tau_c)^{1-h}\sin\frac{\pi}{2}(1 - h)}{(\varepsilon_0 + 2)^2 + 2(\varepsilon_0 + 2)(\varepsilon_\infty + 2)(\omega\tau_\varepsilon)^{1-h}\cos\frac{\pi}{2}(1 - h) + (\varepsilon_\infty + 2)^2(\omega\tau_\varepsilon)^{2(1-h)}}\,. \tag{19}$$

Here h refers to ε^* and assumes for each moment that $h_\alpha = h_\varepsilon$.

Using (9) and (10), we obtain:

$$\alpha'' = \frac{(\alpha_0 - \alpha_\infty)(\omega\tau_\varepsilon)^{1-h}\sin\frac{\pi}{2}(1-h)}{\frac{1-\alpha_\infty}{1-\alpha_0} + 2(\omega\tau_\varepsilon)^{1-h}\cos\frac{\pi}{2}(1-h) + \frac{1-\alpha_0}{1-\alpha_\infty}(\omega\tau_\varepsilon)^{2(1-h)}} . \tag{20}$$

However,

$$\tau_\varepsilon = \tau_\alpha\left(\frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2}\right)^{\frac{1}{1-h}}$$

implies

$$\tau_\varepsilon^{(1-h)} = \tau_\alpha^{(1-h)}\frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2} = \tau_\alpha^{(1-h)}\frac{1-\alpha_\infty}{1-\alpha_0} , \tag{21}$$

and

$$\tau_\alpha^{(1-h)} = \tau_\varepsilon^{(1-h)}\frac{1-\alpha_0}{1-\alpha_\infty} .$$

By multiplying both numerator and denominator of (20) by

$$\frac{1-\alpha_0}{1-\alpha_\infty} ,$$

we arrive at the following expression for α'':

$$\alpha'' = \frac{(\alpha_0 - \alpha_\infty)(\omega\tau_\alpha)^{1-h}\sin\frac{\pi}{2}(1-h)}{1 + 2(\omega\tau_\alpha)^{1-h}\cos\frac{\pi}{2}(1-h) + (\omega\tau_\alpha)^{2(1-h)}} , \tag{22}$$

which is formally identical with ε'', assuming $h_\alpha = h_\varepsilon$.

Up to this point, we have only considered the very simple equations of Debye and Cole–Cole. These equations are followed only by certain dielectric materials. To study the more complicated behavior of polymers and more complex molecules we must refer to the more sophisticated, so-called skewed arcs.

c) Cole–Davidson equations: [12]

Many dielectric relaxations are not symmetrical, and this can be represented in terms of the equation proposed by Davidson and Cole:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + i\omega\tau_\varepsilon)^{\beta_\varepsilon}} \quad \text{with } 0 < \beta_\varepsilon < 1 . \tag{23}$$

In this case, it is not possible to construct an equation similar to (23) for the polarizability in which the paramaters α_0, α_∞, τ_α, and β_α are closely related to the ones appearing in (23), as for example in (21). More specifically, we can only assume that if the permittivity ε^* follows (23), the polarizability seems to follow an equation such as:

$$\alpha^* = \alpha_\infty + \frac{\alpha_0 - \alpha_\infty}{(1 + i\omega\tau_\alpha)^{\beta_\alpha}} , \tag{24}$$

but we cannot insure that $\beta_\varepsilon = \beta_\alpha$ in general.

In summary, the shape of both curves seems to be empirically the same, but the parameters characterizing both equations are not simply related. Thus, we can only transform the empirical results of the real permittivity ε' and loss ε'' into the polarizability α' and loss polarizability α'' by means of (1), and draw information from it about all the parameters appearing in (24), i.e., α_0, α_∞, τ_α, and β_α.

However, we have improved a method to estimate the frequency at which ε'' and $\tan\delta_\varepsilon$ attain a maximum.

From (1), we have

$$\varepsilon^* = \frac{1 + 2\alpha^*}{1 - \alpha^*} , \tag{25}$$

and thus

$$\varepsilon' = \frac{(1 + 2\alpha')(1 - \alpha') - 2\alpha''^2}{(1 - \alpha')^2 + \alpha''^2} , \tag{26a}$$

$$\varepsilon'' = \frac{3\alpha''}{(1 - \alpha')^2 + \alpha''^2} , \tag{26b}$$

and

$$\tan\delta_\varepsilon = \frac{3\alpha''}{(1 + 2\alpha')(1 - \alpha') - 2\alpha''^2} , \tag{26c}$$

where α' and α'' are given by:

$$\alpha' = \alpha_\infty + (\alpha_0 - \alpha_\infty)(\cos\phi_\alpha)^{\beta_\alpha}\cos\beta_\alpha\phi_\alpha , \tag{27a}$$

$$\alpha'' = (\alpha_0 - \alpha_\infty)(\cos\phi_\alpha)^{\beta_\alpha}\sin\beta_\alpha\phi_\alpha , \tag{27b}$$

with

$$\phi_\alpha = \text{arc tan}\ \omega\tau_\alpha .$$

From (26) we can calculate the frequency at which the maximum in ε'' and $\tan\delta_\varepsilon$ appears. After normalizing the first derivatives of ε'' and

$\tan\delta_\varepsilon$, given by (26b) and (26c), to zero, we have:

$$\begin{aligned}&2(1-\alpha_\infty)(\alpha_0-\alpha_\infty)(\cos\phi_\alpha)^{1+\beta_\alpha}\\&\quad-(1-\alpha_\infty)^2\cos(\phi_\alpha(1-\beta_\alpha))\\&\quad-(\alpha_0-\alpha_\infty)^2(\cos\phi_\alpha)^{2\beta_\alpha}\\&\quad\times\cos\{\phi_\alpha(1-\beta_\alpha)\}=0 \qquad (28a)\end{aligned}$$

and

$$\begin{aligned}&(1-\alpha_\infty)(1+2\alpha_\infty)\cos\{\phi_\alpha(1-\beta_\alpha)\}\\&\quad+(1-4\alpha_\infty)(\alpha_0-\alpha_\infty)(\cos\phi_\alpha)^{1+\beta_\alpha}\\&\quad-2(\alpha_0-\alpha_\infty)^2(\cos\phi)^{2\beta_\alpha}\\&\quad\times\cos\{\phi_\alpha(1-\beta_\alpha)\}=0\,. \qquad (28b)\end{aligned}$$

From these equations we obtain by trial ϕ_α and, consequently, ω_ε and τ_ε at the maximum of ε'' and $\tan\delta_\varepsilon$.

Conversely, from (4), (5), and (6) giving α', α'' and $\tan\delta_\alpha$ in terms of ε' and ε'', we can, by an identical procedure, obtain the frequencies at which α'' and $\tan\delta_\alpha$ attain a maximum.

The corresponding equations are:

$$\begin{aligned}&(\varepsilon_\infty+2)^2\frac{\cos\{\phi_\varepsilon(1+\beta_\varepsilon)\}}{(\cos\phi_\varepsilon)^{1+\beta_\varepsilon}}\\&\quad+2(\varepsilon_0-\varepsilon_\infty)(\varepsilon_\infty+2)\\&\quad+(\varepsilon_0-\varepsilon_\infty)^2\frac{\cos\{\phi_\varepsilon(1-\beta_\varepsilon)\}}{(\cos\phi_\varepsilon)^{1-\beta_\alpha}}=0 \qquad (29a)\end{aligned}$$

and

$$\begin{aligned}&(\varepsilon_\infty-1)(\varepsilon_\infty+2)\frac{\cos\{\phi_\varepsilon(1+\beta_\varepsilon)\}}{(\cos\phi_\varepsilon)^{1+\beta_\varepsilon}}\\&\quad+(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_\infty+1)\\&\quad+(\varepsilon_0-\varepsilon_\infty)^2\frac{\cos\{\phi_\varepsilon(1-\beta_\varepsilon)\}}{(\cos\phi_\varepsilon)^{1-\beta_\alpha}}=0\,. \qquad (29b)\end{aligned}$$

The validity of both sets of Eqs. (28) and (29) is only restricted by the validity of (23) in representing dielectric and polarizability properties of the material.

d) Havriliak and Negami equation: [13]
Finally, we consider the widely used empirical equation of Havriliak and Negami to represent many relaxations in polymers and complex systems. The equation proposed by these authors is a generalization of the model proposed by Cole–Cole and Davidson–Cole, i.e.:

$$\varepsilon^*=\varepsilon_\infty+\frac{\varepsilon_0-\varepsilon_\infty}{(1+(\mathrm{i}\omega\tau_\varepsilon)^{1-h_\varepsilon})^{\beta_\varepsilon}}\,. \qquad (30)$$

As assumed previously, ε^* fits to an H–N skewed arc; α^* fits also, but with different parameters not easily related to the ε representation. According to this, we have:

$$\alpha^*=\alpha_\infty+\frac{\alpha_0-\alpha_\infty}{(1+(\mathrm{i}\omega\tau_\alpha)^{1-h_\alpha})^{\beta_\alpha}}\,, \qquad (31a)$$

$$\alpha'=\alpha_\infty+(\alpha_0-\alpha_\infty)r^{-\beta_\alpha/2}\cos\beta_\alpha\phi_\alpha\,, \qquad (31b)$$

$$\alpha''=(\alpha_0-\alpha_\infty)r^{-\beta_\alpha/2}\sin\beta_\alpha\phi_\alpha\,, \qquad (31c)$$

$$\begin{aligned}r=&\left(1+(\omega\tau_\alpha)^{1-h_\alpha}\sin\frac{\pi h_\alpha}{2}\right)^2\\&+\left((\omega\tau_\alpha)^{1-h_\alpha}\cos\frac{\pi h}{2}\right)^2, \qquad (31d)\end{aligned}$$

where

$$\phi_\alpha=\mathrm{arc\ tan}\frac{(\omega\tau_\alpha)^{1-h_\alpha}\cos\frac{\pi}{2}h_\alpha}{1+(\omega\tau_\alpha)^{1-h_\alpha}\sin\frac{\pi}{2}h_\alpha}\,.$$

By a procedure identical to that in the last section, we have, after equalizing the first derivatives of ε'' and $\tan\delta_\varepsilon$ expressed in terms of α' and α'' to zero, the following two expressions:

$$\begin{aligned}&(1-\alpha_\infty)^2\cos\left(\beta_\alpha\phi_\alpha+\frac{\pi}{2}h_\alpha\right)\\&\quad-2(1-\alpha_\infty)(\alpha_0-\alpha_\infty)r^{-\beta_\alpha/2}\cos\frac{\pi}{2}h_\alpha\\&\quad+(\alpha_0-\alpha_\infty)^2r^{-\beta_\alpha}\cos\left(\beta_\alpha\phi_\alpha-\frac{\pi}{2}h_\alpha\right)\\&\quad-(\omega\tau_\alpha)^{1-h_\alpha}\{(1-\alpha_\infty)^2\\&\quad-r^{-\beta_\alpha}(\alpha_0-\alpha_\infty)^2\}\sin\beta_\alpha\phi_\alpha=0\,, \qquad (32a)\end{aligned}$$

$$\begin{aligned}&(1-\alpha_\infty)(1+2\alpha_\infty)\cos\left(\beta_\alpha\phi_\alpha+\frac{\pi}{2}h_\alpha\right)\\&\quad+(1-4\alpha_\infty)(\alpha_0-\alpha_\infty)r^{-\beta_\alpha/2}\cos\frac{\pi}{2}h_\alpha\\&\quad-2(\alpha_0-\alpha_\infty)^2r^{-\beta_\alpha}\cos\left(\beta_\alpha\phi_\alpha-\frac{\pi}{2}h_\alpha\right)\\&\quad-(\omega\tau_\alpha)^{1-h_\alpha}\{(1-\alpha_\infty)(1+2\alpha_\infty)\\&\quad+2(\alpha_0-\alpha_\infty)^2r^{-\beta_\alpha}\}\sin\beta_\alpha\phi_\alpha=0\,. \qquad (32b)\end{aligned}$$

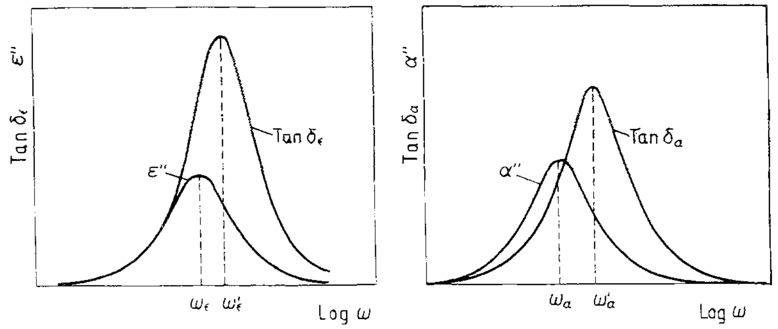

Fig. 1. Generic representations of the dielectric loss permittivity and loss tangent (ε'', $\tan\delta_\varepsilon$), and of the dielectric loss polarizability and the corresponding tangent (α'', $\tan\delta_\alpha$) as a function of the frequency. The frequencies at the respective four maxima corresponding to a Debye semicircle are:

$$\omega_\varepsilon = \tau_\varepsilon^{-1}$$

$$\omega'_\varepsilon = \left(\frac{\varepsilon_0}{\varepsilon_\infty}\right)^{1/2} \omega_\varepsilon$$

$$\omega_\alpha = \frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2}\,\omega_\varepsilon$$

$$\omega'_\alpha = \left(\frac{\varepsilon_\infty(\varepsilon_0 - 1)(\varepsilon_0 + 2)}{\varepsilon_0(\varepsilon_\infty - 1)(\varepsilon_\infty + 2)}\right)^{1/2} \omega'_\varepsilon$$

To solve these equations for ϕ_α, we must first calculate α_0, α_∞, β_α, h_α and τ_α (the last parameter is the relaxation time at which $\omega\tau_\alpha = 1$, and not that corresponding to the maximum). This can be carried out by the standard procedure from α'' as a function of α'.

After solution by trial and error we obtain the frequencies at which ε'' and $\tan\delta_\varepsilon$ attain a maximum. These can be compared to the frequencies at which α'' and $\tan\delta_\alpha$ reach a maximum.

Examples

In this section, we apply our results to some experimental data in the literature.

a) First we consider dielectric data of Vn_2S_2/TCNQ from [8].

The dielectric loss permittivity and loss tangent permittivity are given in Fig. 2 at 7 °C and − 10 °C, in a range of frequencies between 20 and 10^5 Hz. We have selected from the experimental data only these two curves for our purposes. The corresponding loss polarizability and loss tangent polarizability are shown in Fig. 3. In Fig. 2 we observe only a shoulder in the ε'' curve, but α'' in Fig. 3 shows a well separated relaxation. The α'' vs α' curve exhibits (Fig. 4) behavior corresponding to a Cole–Cole equation; however, at lower frequencies we observe a new relaxation (which is observed at higher temperatures, separated from the main relaxation). The characteristic parameters are given in the first row of Table 1.

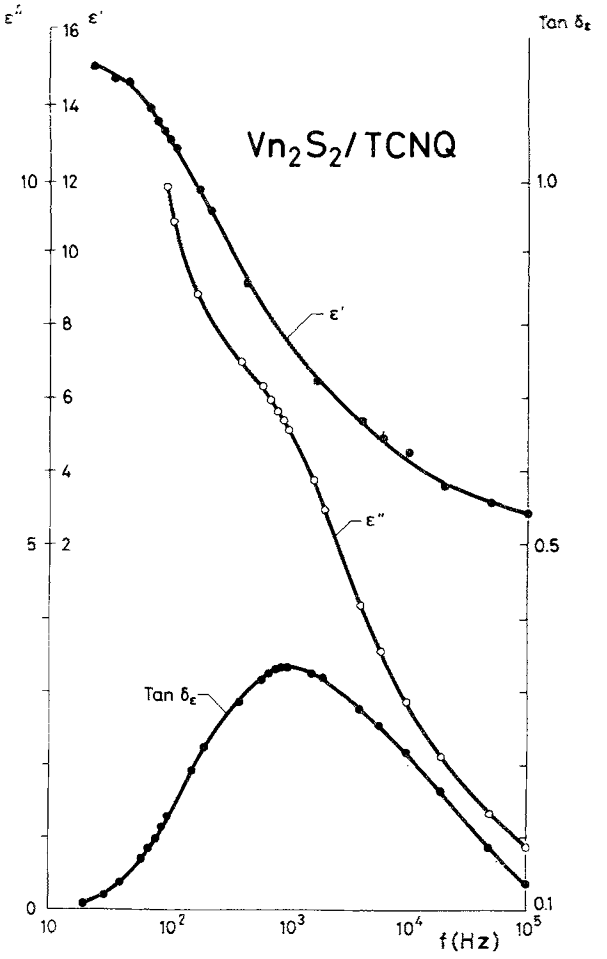

Fig. 2. Dielectric loss at 7 °C (○) and dielectric permittivity and $\tan\delta_\varepsilon$ (●) at − 10 °C for Vn_2S_2/TCNQ complex

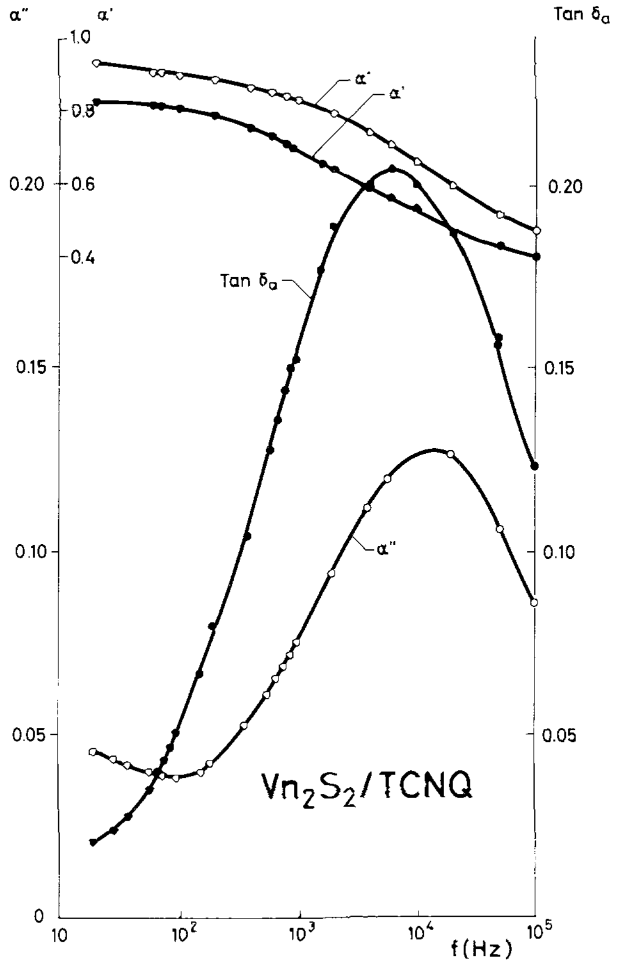

Fig. 3. Dielectric polarizability α' and loss polarizability α'' (○) at 7 °C and dielectric polarizability α' and $\tan\delta_\alpha$ (●) at − 10 °C for Vn_2S_2/TCNQ complex

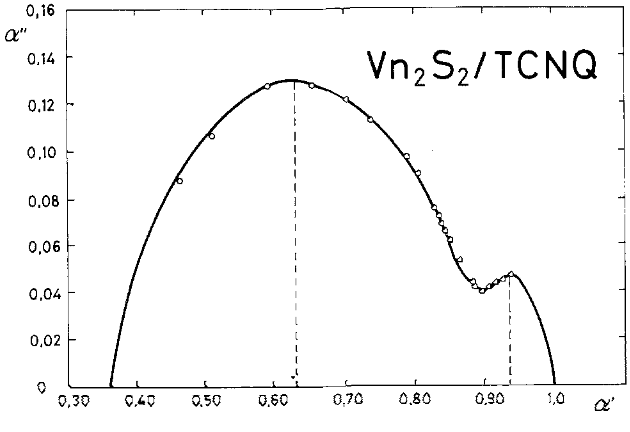

Fig. 4. Cole–Cole plot for α'' vs α' for Vn_2S_2/TCNQ at 7 °C. A new relaxation peak can be seen at low frequency

Table 1

			(a)	(a)	(b)	(b)	(b)
T (°C)	α_0	α_∞	$f_{\varepsilon \max}$	$f_{\alpha \max}$	ε_0	ε_∞	$1-h$
7	0.90	0.36	–	1.5×10^4	28	2.69	0.564
−10	0.84	0.34	1.0×10^3	5.0×10^3	16.75	2.55	0.612

(a) $f\,(\mathrm{Hz}) = \omega/2\pi$
(b) calculated from Eqs. (7a) and (7b)

We have used the equation

$$\alpha''_{\max} = \frac{1}{2}(\alpha_0 - \alpha_\infty)\tan\frac{\pi}{4}(1-h) \qquad (33)$$

to calculate $1-h$ in the last column, and a similar equation to calculate $\varepsilon''_{\max}$ (see [10], p. 116).

From (16) we obtain $f_\varepsilon = f_\alpha/27 = 560$ Hz, which is a very reasonable value.

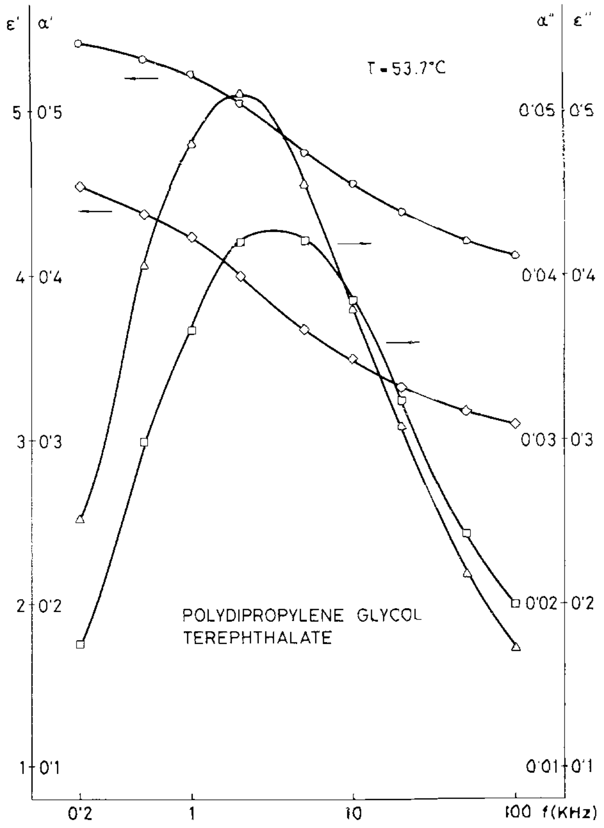

Fig. 5. Real and imaginary parts of the complex dielectric permittivity and polarizability for polydipropylene glycol terephthalate at 53'7 °C. (◇ and △ for ε' and ε'', respectively, ○ and □ for α' and α'', respectively)

Loss tangent data can be useful for testing our calculations. In this case it is easier to estimate the parameters of the relaxation. Moreover, from Fig. 2 we may estimate the frequency at which $\tan \delta_\varepsilon$ attains a maximum value ($f \cong 10^3$ Hz). According to the values of Table 1 and by (17), we obtain $f = 1.1 \times 10^3$ Hz for the $\tan \delta_{\varepsilon\max}$, very close to the experimental value.

b) Now we consider a relaxation related to the glass-rubber transition of an amorphous polymer, poly-dipropylene glycol terephthalate [14]. In Fig. 5 the real and imaginary parts of the complex permittivity at 53.7 °C are shown. It is obvious that there is no question concerning f at $\varepsilon''_{\max}$ or at $\tan \delta_{\varepsilon\max}$ Here we intend only to improve the proposed method for the Havriliak–Negami equation, and to compare the calculated values with the experimental ones. Thus, the calculated components of the complex polarizability, α' and α'' are also shown in Fig. 5. Characteristic values for the skewed arc α'' vs α' are $\alpha_0 = 0.550$, $\alpha_\infty = 0.380$, $1\text{-}h_\alpha = 0.890$, $\beta_\alpha = 0.400$ and $\tau_\alpha = 1.324 \cdot 10^{-4}$ s.

By trial and error, from Eq. (32a) we obtain a value of 1980 Hz for the frequency at the maximum of ε'', very close to the observed value (see Fig. 5). The ratio of the characteristic relation time is 2.09, this value being the relative shift of α with reference to the ε spectra along the frequency axis.

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Authors' address:

R. Díaz Calleja
Laboratory of Thermodynamics and Physical Chemistry
of E.T.S.I.I.V. Valencia
Apartado 22012
46071 Valencia, Spain