INFLUENCE OF IODINE ON LOW FREQUENCY DIELECTRIC PROPERTIES OF ANTHRONE

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

Low frequency dielectric properties of polycrystalline anthrone and anthrone/iodine charge-transfer complex are presented. Polycrystalline anthrone proves to be a typical low-loss material. Iodization of anthrone pellets leads to a remarkable change in dielectric properties. Dielectric response of anthrone/iodine CT complex shows comparatively strong low frequency dispersion. The change in dielectric properties proves to be reversible to great extend as removing of iodine by heating at 373 K for a few hours almost completely restores the dielectric values of a virgin anthrone sample.

Low frequency dispersion (LFD) is a kind of dielectric response found frequently in materials in which the dielectric properties are dominated by either electronic[1–3] or ionic[4,5] charge carriers. In this paper an experimental evidence of LFD in anthrone/iodine charge-transfer (CT) complex is presented. It is shown that the low frequency dielectric properties of the CT complex differs significantly from the properties of anthrone which is a typical low loss material.

The dielectric properties of materials can be described by its complex capacitance

$$C^* = C' - iC'' = C(\omega) - iG(\omega)/\omega \quad , \qquad (1)$$

where C is the ordinary electric capacitance and $G(\omega)$ is the conductance, which is the sum of the AC conductance $\sigma_{AC}(\omega)$ and the DC conductance G_0. The complex susceptibility can be written in the form:

$$\chi^*(\omega) = \chi'(\omega) - i\chi''(\omega) = G_f[C(\omega) - C_\infty - i(G(\omega)/\omega - G_0/\omega)] \ , \tag{2}$$

where G_f is a geometrical factor, C_∞ is the "high frequency" capacitance and G_0 is the direct current conductance.

The relation between the real and imaginary part of complex capacitance is given by Kramers–Kronig (KK) equations[1,6]:

$$C'(\omega) = C(\omega) = C_\infty + \frac{2}{\pi}\int_0^\infty \frac{G(x) - G_0}{x^2 - \omega^2}\,\mathrm{d}x \tag{3a}$$

$$C''(\omega) = G(\omega)/\omega = G_0/\omega + \frac{2\omega}{\pi}\int_0^\infty \frac{C(x) - C_\infty}{\omega^2 - x^2}\,\mathrm{d}x \ . \tag{3b}$$

The above relations results from the causality and the linearity of the system. In this situation the KK relations are valid for most of dielectric substances including bulk dielectric response of polycrystalline organic molecular compounds. Despite this the investigation of KK compatibility of the two components of the complex capacitance is often fruitful when analysing the results of dielectric measurements. In particular, it enables one to estimate the influence of DC conduction on the results of dielectric measurements. When we have to do with the power frequency dependence of the AC conduction

$$G_{AC}(\omega) \propto \omega^n \ , \tag{4}$$

which dominates the dielectric response in the frequency range of a few decades then the relation between the imaginary and real part of the dielectric susceptibility (and capacitance on the assumption of negligible influence of DC phenomena) is given by

$$C''/(C - C_\infty) = \chi''(\omega)/\chi'(\omega) = \mathrm{cotg}\,(n\pi/2) \ . \tag{5}$$

The distance between the straight lines in the double logarithmic plot resulting from the KK relations is equal to log cotg ($n\pi/2$). In this case, estimation of compatibility of the $C - C_\infty$ and G/ω curves is very easy and consists of measuring the distance between the two curves in the double logarithmic plot.

The typical spectral shape of LFD dielectric response in the frequency domain is shown in Fig. 1*a*. Both C' and G/ω curves consist of two straight lines of different slopes. The response may be well described by the power law:

$$C^*(\omega) = A_h(i\omega)^{n-1} + A_l(i\omega)^{p-1} \ , \qquad (6)$$

where n describes the high-frequency part of the response (n is smaller but usually close to 1) and p describes the low-frequency one with p positive but close to zero.

The time-domain response of a system showing LFD is presented in Fig. 1*b*. The discharging currents are characterized by a very slow decay with time. The slope of $i_d(t)$ curve results from Fourier transform of the frequency power law and is equal to $-n$ for the short times and to $-p$ for the time longer then $t_0 = 1/\omega_0$.

As it has been mentioned above LFD is considered to be a special type of dielectric response characteristic of comparatively well conducting materials in which the dielectric properties are dominated by moving charge carriers. Three possible explanations of this phenomenon have been suggested so far. The explanations will be mentioned in the next part of this paper.

EXPERIMENTAL

The dielectric measurements presented in this paper were carried out with Solartron Frequency Response Analyser in the frequency range 10^{-3}–10^5 Hz. The samples were prepared as follows: compressed polycrystalline anthrone pellets were kept in iodine vapour for about 2 weeks at the room temperature. Charge-transfer (CT) anthrone/iodine complex was the result of the iodization[7]. Then gold electrodes were evaporated in vacuum of the order of 10^{-5} Torr. The thickness of pellets was about 1 mm, their diameter was about 12 mm. The electrode area was about 80 mm^2. The dielectric measurements were carried out a few days after evaporation of electrodes.

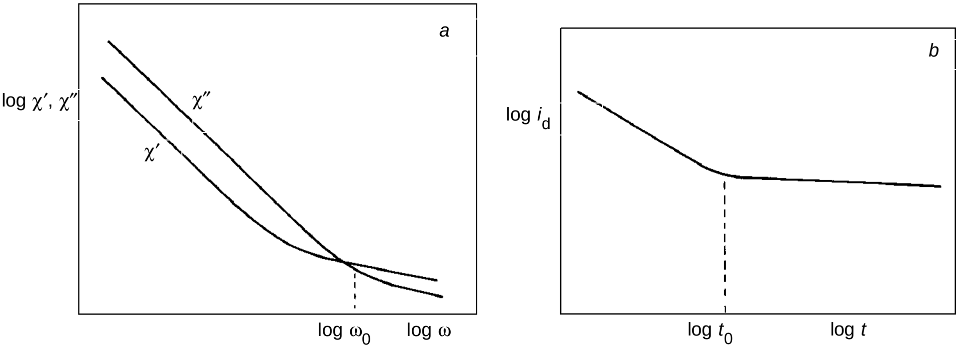

FIG. 1
The functional form of the dielectric response showing low frequency dispersion. *a* Frequency-domain response, *b* time-domain response. $t_0 = 1/\omega_0$ is the transition time between the high-frequency and low-frequency part of the response

RESULTS AND DISCUSSION

Figure 2 shows the dielectric response of anthrone/iodine CT complex at 195 K, 272 K and 297 K. As we see the complex is a low-loss material at the low temperatures, but at the room temperature (297 K) a comparatively strong low frequency dispersion takes place. The low-frequency dielectric properties of anthrone/iodine complex differs significantly from the properties of anthrone (see Fig. 3) which is a typical low-loss material like most of simple aromatic hydrocarbons[8–10]. When the anthron/iodine system is annealed at 373 K for a few hours the iodine escapes from the sample and the pellet becomes a typical low-loss material (see Figs 2*b* and 3). The dielectric response of annealed samples is very similar to the response of polycrystalline pure anthrone (see Fig. 3). In order to confirm the influence of iodine on the dielectric properties of anthrone the annealed samples were iodized again by keeping once more in iodine vapour for a few days. The dielectric measurements were carried out immediately after removing the sample from the iodine atmosphere. Figure 4 shows the dielectric properties of the reiodized sample. As we see a strong LFD has been detected in the sample. If we subtract $C_\infty = 8 \cdot 10^{-12}$ F resulting from the high-frequency dielectric phenomena we get $C - C_\infty$ and G/ω stright lines parallel to each other within about 5 orders of magnitude. The slope of both $C - C_\infty$ and G/ω lines is between –0.98 ÷ –0.99. This means that according to Eq. (5) the distance between the lines should be equal to 1.5 ÷ 1.8 decades if we assume that the dc conduction is negligible. The distance found from

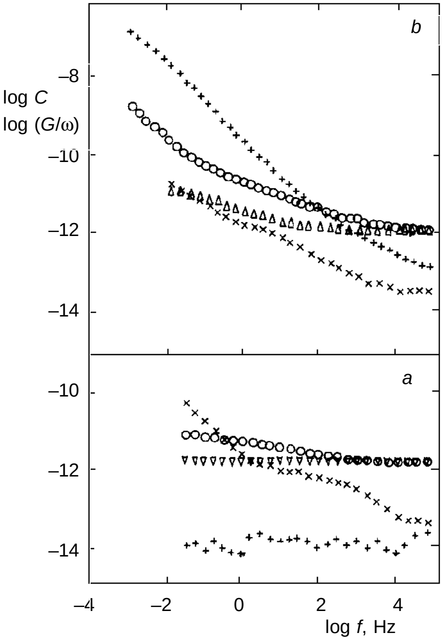

FIG. 2
The dielectric response of anthrone/iodine CT complex at various temperatures. *a* T = 195 K: ∇ C, + G'/ω; T = 273 K: ❍ C, × G/ω. *b* 297 K; virgin sample: ❍ C, + G/ω; the sample after annealing for a few hours at 373 K. Δ C, × G/ω. C and G/ω in F

experimental results (Fig. 4) equals to about 1.6 decades. This suggests that the direct current conduction is not a dominant factor in the dielectric response though some influence of DC conduction cannot be excluded. The above conclusion is in a good agreement with the data shown in Fig. 5. The conduction found from Fig. 4 may be estimated to be about $G(\omega) \approx \text{const} \approx 6 \,.\, 10^{-9}$ S, while the DC conduction resulting from Fig. 5 is equal to about $2.5 \,.\, 10^{-9}$ (the charging current is almost time independent so it may be assumed that G_{DC} = current/voltage), i.e. the DC conduction is twice as small as the AC one.

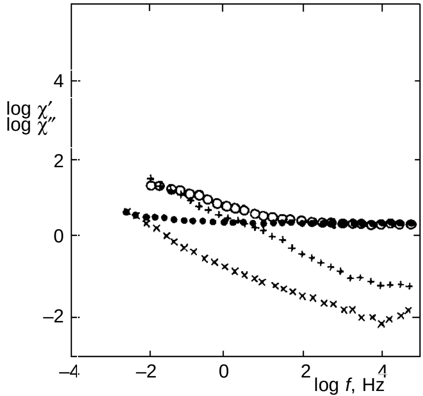

FIG. 3

The dielectric response of anthrone polycrystalline layer at the room temperature (297 K). ● χ′ (real part of dielectric susceptibility), × χ″ (imaginary part of dielectric susceptibility). For easier comparison the data from Fig. 2*b* for annealed anthrone/iodine CT complex are also shown. ❍ χ′, + χ″

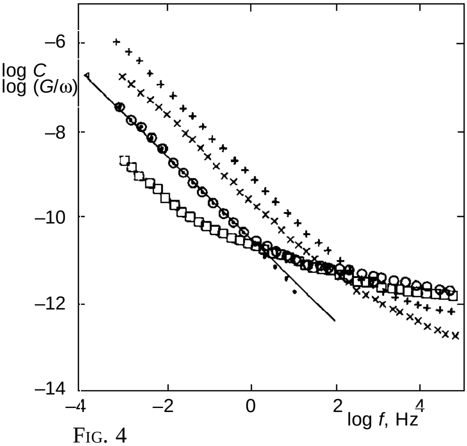

FIG. 4

The dielectric response of the reiodized anthrone sample at the room temperature (297 K). ❍ *C*, + *G*/ω, ● $C - C_\infty$ with $C_\infty = 8 \,.\, 10^{-12}$ F. For easier comparison the data from Fig. 2*b* for virgin anthrone/iodine CT complex are also shown. ❐ *C*, × *G*/ω

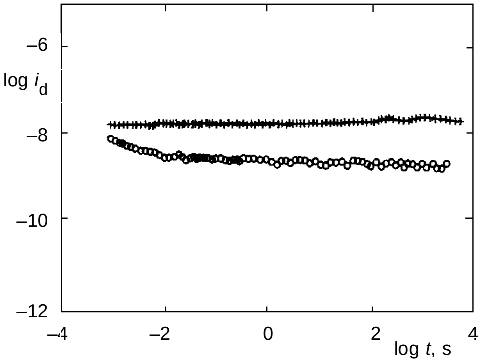

FIG. 5

The polarisation (+) and depolarisation (❍) currents under a step-function potential excitation at the room temperature (297 K). *U* = 5 V, i_d in A

The existence of such strong LFD suggests that a comparatively efficient long-time storage of charge takes place. The above conclusion has been confirmed with measurements of depolarisation currents in the reiodized samples. Figure 5 shows the polarisation and depolarisation currents obtained by application of step potential. As we see a very slow decay of depolarisation has been detected. Let us note that the transition frequency ω_0 defined in Figs 1*a* and 1*b*, found from both frequency (Fig. 4) and time (Fig. 5) response is equal to about 10^2 Hz.

It has been suggested that LFD in organic molecular solids may be interpreted in terms of Maxwell–Wagner–Sillars polarisation phenomena[11]. Two other possible explanations of LFD have been put forward so far. The first one is an electrochemical model proposed by Jonscher[12], but the applicability of the model is limited to ionic conductors, so the model in its present form rather could not be used for systems dominated by electronic charge carriers like CT organic complexes. The second one is Dissado–Hill model[13] which is a version of their general many-body theory of dielectric response of solids. Whether the model might be used for organic molecular crystals is still an open question.

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