The dielectric absorption phenomena in sodium acetylacetonate compound

A Sawaby, H H Afify and A A Shabaka

Department of Physics, National Research Centre, Dokki, Cairo, Egypt

Abstract : Electrical conduction of sodium acetylacetonate compound [Na(ac, ac)] was measured as a function of temperature, field and time. The current-time characteristic have been studied in the voltage range 2-100 volt and in the temperature range 20-100°C. The i-v characteristic and dc conductivity were also studied and discussed on the basis of ionic conduction. The current-time tendency after an application of dc voltage as well as the current maximum observed by the reversal of applied voltage polarity are discussed in the light of the orientation of electric dipole and space-charge mechanisms. The obtained results made it possible to determine a set of conduction parameters including carrier mobility μ, mobile ion density, n, and activation energy of the conduction E_a.

Keywords : Dielectric absorption phenomena, sodium acetylacetonate compound, conduction mechanism, current-time and current-voltage characteristics.

PACS Nos : 72.15.−v, 72.80.−r

1. Introduction

Although many investigations have been made on acetylacetone as a good chelating agent and as solvent for electrochemistry measurements (Khera *et al* 1983), less have been made on electrical properties of metal acetylacetonate. The dielectric constant, dielectric loss, pyroelectric behaviour and dipole moment of some of these compounds such as Fe, Al, Cu, Na, and K acetylacetonate were previously studied (Sahai and Verma 1981, Molokhia 1986, Kamel *et al* 1975, Amin *et al* 1980, Kadry *et al* 1984). However, the available data is still far from being complete.

The present work is devoted to investigate and study the effect of dc applied voltage and temperature on the current time and current-voltage characteristics of sodium acetylacetonate compound [Na(ac, ac)] to obtain some information about the electrical behaviour and conduction mechanism of this compound.

422

2. Experimental technique

Sodium acetylacetonate compound was prepared by a conventional method (Lowis et al 1984). The purity of the sample was confirmed from different methods of observations such as IR spectra and melting point. The powder of [Na(ac, ac)] was compressed at 200 k bar/cm², in the form of discs (1.2 cm diameter and 1.7 mm thickness).

For electrical measurements, the disc was sandwitched between two copper electrodes using a specially designed holder. The electrode surfaces were previously polished to optical quality to ensure good electrical contact. A high impedence electrometer (VA-J52, Dresden DDr) and a multiflex galvanometer type MG2, through a conventional electrical circuit were used for measurements.

3. Experimental results

The relation between current and time (I-t curves) of Na(ac, ac) for different applied dc voltage in one direction at 60°C is shown in Figure 1. The time dependence
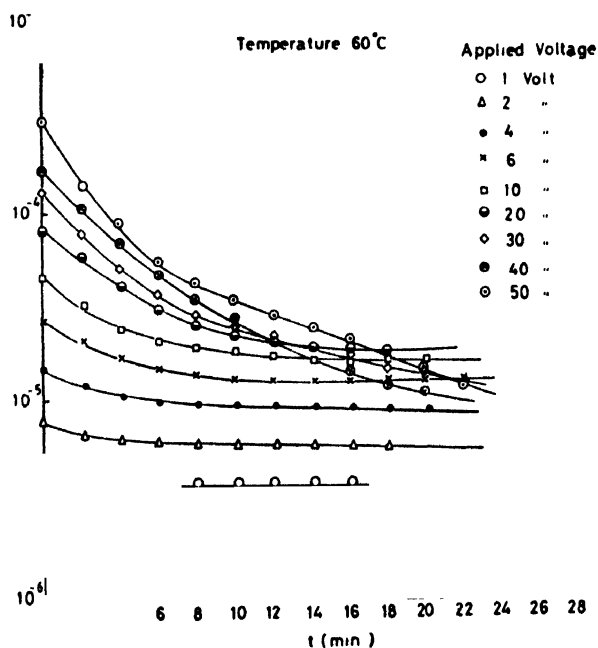

Figure I. (I-t) Relation at different voltage.

of current at voltage up to 5 ± 1 volt could be negligible, but it becomes obvious at voltage above 8 volts and their gradient tends to increase with volt. The ten volts are selected to be appropriate for studying the I-t relation at different

temperatures as shown in Figure 2.   The I-t behaviour becomes clearer as the tem-
perature rises.   The I-V plots in log-log scale for the Na (ac, ac) samples are shown
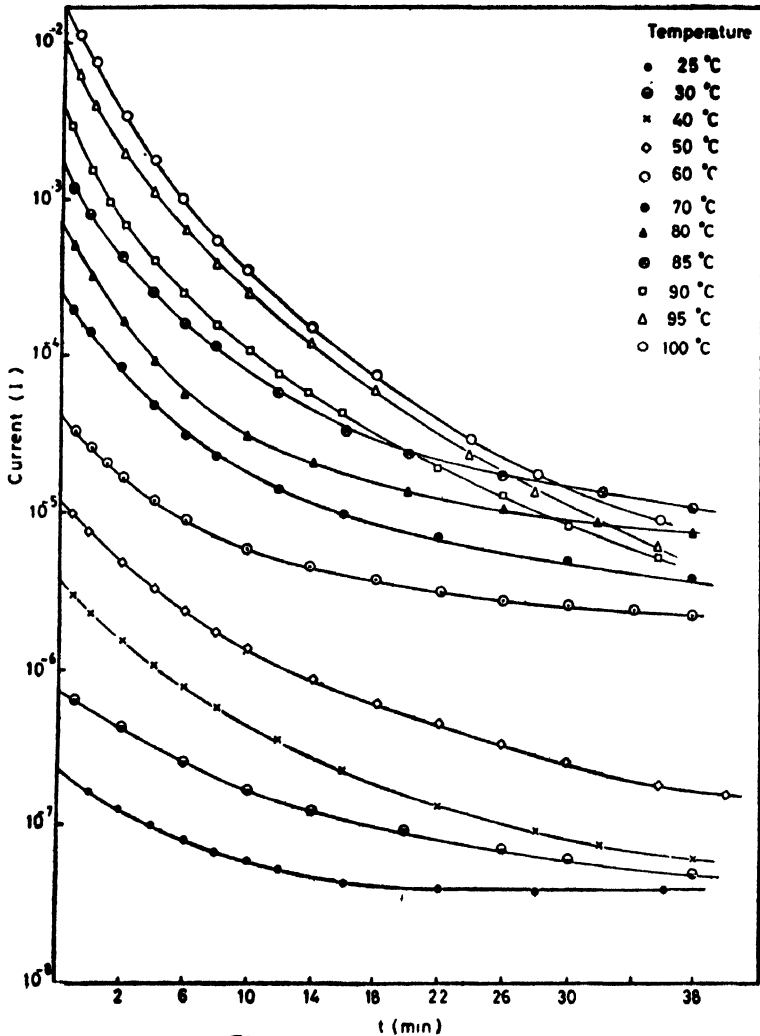

Figure 2.   (I-t) Relation at different temperatures.

in Figure 3.   For curve (a), where the current was measured at one direction of
applied voltage, at first the plots are ohmic but show a deviation above 10 volts.
For curve (b), the polarity of the applied voltage was reversed and the current was
measured as a mean value of the current before and after the reversing process of
the applied voltage. With this condition, a straight line is obtained as shown clearly
in the figure.   However, the reversing process of the applied voltage polarity is also
used for the derivation of the dc conductivity σ at different temperature. The results
are compared with the apparent dc conductivity obtained from two minutes
current after application of the dc voltage in one direction as shown in Figure 4. The

log σ and $10^3/T$ relation gives straight parallel lines for the above two conditions and the calculated activation energy is found to be 1.65 eV. The I-t curves before
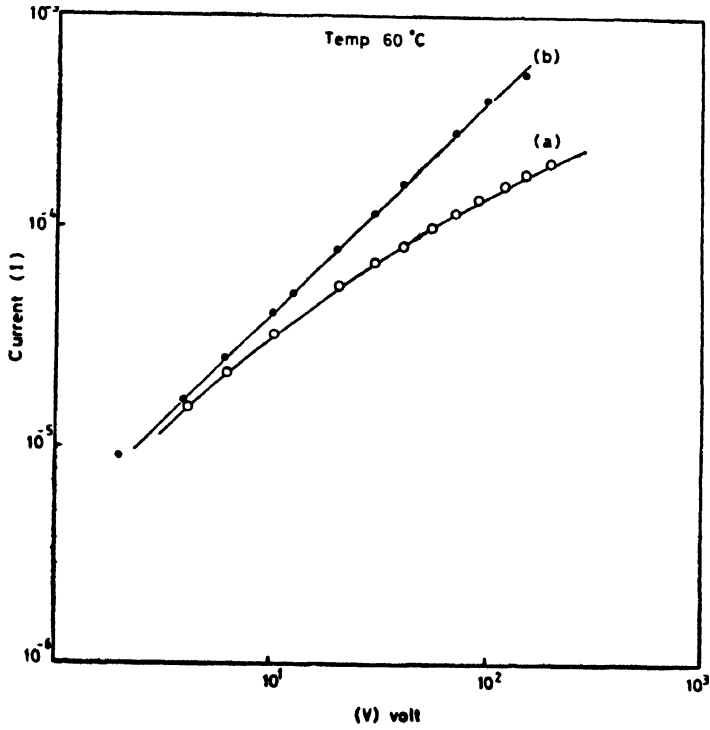

Figure 3. (I-V) characteristics of Na (ac, ac).
(a) Direct (polarized). (b) Unpolarized.

and after reversal of voltage polarity (20 volts) at different temperatures are given in Figure 5. Here, the first voltage application to the sample brings about the current change with time similar to that of the curves in Figure 2. However, the I-t curves after reversing polarity after 30 minutes are completely different. The I-t curves at 50°C go down monotonically at an initial application of voltage, but it

Table I. The calculated mobility and ion density corresponding to the maximum current at each temperature.

I_{max}	$t°C$	t_{sec}	$\mu_\theta = l^2/tv \ cm^2$ $v^{-1}.sec^{-1}$	$n = \frac{I_{max}}{q\mu E}$ (cm^{-3})
5×10^{-5}	50	140	1.03×10^{-5}	2.0×10^{17}
2×10^{-4}	60	120	1.20×10^{-5}	9.0×10^{17}
1×10^{-3}	70	090	1.60×10^{-5}	3.0×10^{18}
6×10^{-3}	80	070	2.06×10^{-5}	1.6×10^{19}
6×10^{-2}	90	050	2.89×10^{-5}	1.1×10^{20}

has a current maximum at about 140 seconds, after the reversal of polarity. The hump turns to be clearer as the temperature rises. The time corresponding to the
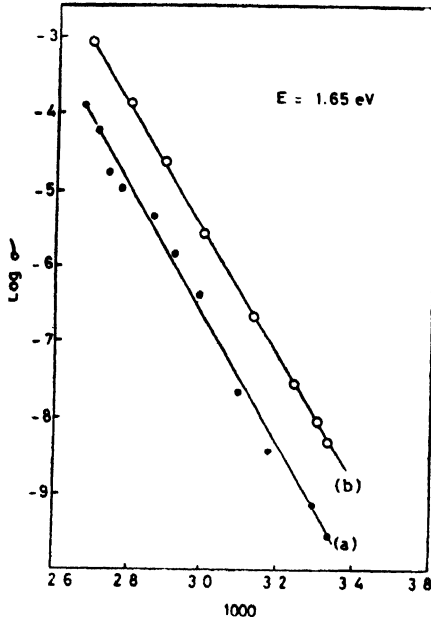

Figure 4. Log $V, 10^3/T$.
(a) two minutes after volt application.   (b) mean value of current before and after reversing the applied voltage.

current peak as well as the calculated ion mobility and ion density at each working temperature are given in Table 1.

4. Discussion

When a dc voltage is applied to liquid or solid dielectric, a current-time dependency is observed. This phenomenon is well known as dielectric absorption. An absorption current usually superposes on equilibrium leakage current at an application of dc voltage polymers, and therefore, I-t curves in many cases change for a considerably long period (Munick 1956). Also, the I-t curves of PVC show characteristic changes in the glass transition around 80°C ; below this temperature the I-t curves do not attain the leakage current even at two hours after the application of dc voltage but they are regarded to be equilibrium leakage current within about 10 minutes at 90°C (Ieda *et al* 1968). The first component of the absorption current is related to the relaxation process of dipole orientation in PVC (Oster 1967).

On the contrary I-t curves of the investigated samples shown in Figure 2 appear to have an equilibrium leakage current at nearly room temperature and the time dependence of current becomes clearer as the temperature rises. However,

there are two mechanisms (Kosoki *et al* 1970), to explain the I-t curves of (Na, acac) compound :

1. An effective decrease in the density of the mobile ions with the specimen due to their arrival at the electrode (clean-up effect).

2. An effective drop of the electric field strength in the bulk of the specimen due to the space-charge effect of the accumulated ions at the electrodes.

Since these two mechanisms are directly related to the ion drift velocity, their effect on the conduction current may be intensified with temperature by an enhancement of mobility. The measured current, $I_{(t)}$, could be given by

$$I_{(t)} = qn\mu E^*$$ (1)

where *n* is the ionic density, E^* the effective field-strength in the specimen bulk, *q* the ionic charge and μ is the ionic mobility. This equation assist the explanation of current-time dependence. According to two preceding mechanisms, *n* and E^* are decreased with time after application of field on the sample. Therefore, the current will decrease with time. Thus, the first component of I-t curve in Figure 2 may be explained by the dependence of ion density *n* and the effective electric field-strength E^* on time. On the other hand, the I-V characteristics of the investigated sample show that the ohmic law is valid when the current is taken as a mean value before and after the reversal of the applied voltage polarity (to avoid the polarization effect), or by measuring the current after a fixed short-time (2 minutes) of applied voltage in one direction. Under these two conditions for measuring the current, the temperature dependence of electrical conductivity σ is found to follow the wellknown relation

$$\sigma = \sigma_0 \exp(-E_0/KT).$$

The activation energy E_0 was calculated and found to be 1.65 eV. This value is in good agreement with that obtained for the ionic conduction mechanism in some organic materials (Amborski 1962, Jain *et al* 1978, Jonscher 1967). Therefore, the obtained E_0 (1.65 eV) for Na (ac, ac) may be in favour of ionic conduction mechanism. The deviation of I-V curves from Ohm's law above 10 volts may be due to an ionic layer built-up near electrodes.

For having an idea about the situation of the drifted ions to the vicinity of the electrodes, the polarity of the applied voltage is reversed after 30 minutes application dc voltage in one direction. The I-t curves given in Figure 5 not only show clearly the current-peak as the temperature rises but also the decrease of the time corresponding to the current-peak at each temperature. The values are given in Table 1. A similar phenomenon has been observed in the I-t curves of some oils for electrical insulation (Nakajima 1960) and high plasticized PVC (Ieda and

Shiunohara 1962). The following mechanism could be used to explain the I-t hump in Figure 5. Generally, the ion density in dielectrics is determined by three factors ; dissociation, recombination and dissipated ion at electrodes. The movable ions for the investigated samples are supplied by the thermal decomposition of Na (ac, ac). Supposing the rate of creation of ion due to the dissociation is
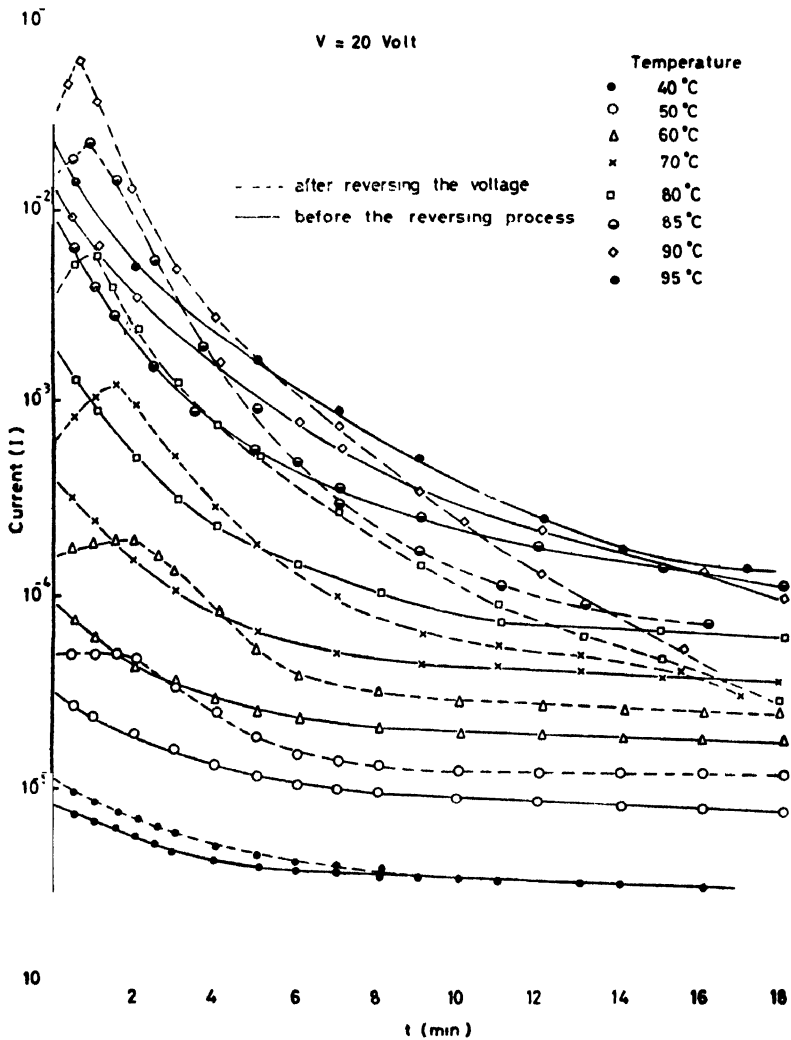

Figure 5. (I-t) Relation before and after reversing the applied voltage.

smaller to that of dissipation of ion due to the clean-up action of current and the recombination, the movable ions decrease and the current diminishes subsequently. If the voltage polarity is reversed in this situation, it is expected that just after the reversal, the ion density is maintained and current gives the opposite direction, but the same value with that just before the reversal and the ions collected near electrodes or deposited at electrodes diffuse towards the opposite electrode. Then,

it may be considered that the current increases till t_{max} when the ion density arrives at a maximum value and successively decreases, because ions gather at the opposite electrode again. Since this process is related to ion velocity, the larger the ion mobility and applied voltage, the shorter the t_{max} can be provided. Time of flight of ions between electrodes can be correlated to ion mobility (Rose 1955) by using

$$\tau = l^2/\mu_e V \tag{2}$$

where l is the distance between electrodes (sample thickness), μ_e ion mobility and V is the applied voltage. Thus, only as a first approximation disregarding the distortion of the electric field caused by the space-charges of the ionic layer, τ might be correlated to t_{max} in l-t curves in Figure 5. Then eq. (2) will be

$$t_{max} = l^2/\mu_e V. \tag{3}$$

Hence, ion mobility μ_e could be estimated from t_{max} in eq. (3) as well as ion density from l_{max} by using the eq. $l = nq\mu E$. The calculated values for μ_e and ion density n together with l_{max} at each working temperature are given in Table 1. The ion density shows a thousand time increase in the temperature range from 50°C to 100°C while the mobility has a slight increase. Also, (Chutia and Barva 1980) had observed a slight change in ion mobility by increasing the test temperature from 15°C to 80°C for polyvinyl acetate films.

The number of ions accumulating near the electrode, n, at the dc voltage application in one direction during time interval between $t=0$ and $t=t$ per unit area, is obtained from Faraday's law

$$n = \int_0^t i \, \frac{dt}{q}.$$

Assuming that the density of mobile ions in the bulk at $t=0$ is n_0, the mobile ion density n_t in the bulk at $t=t$ could be given by $n_{(t)} = (n_0 - n)/l$. Therefore, the current l at time t is given by

$$l = q\mu E \left(n_0 - \int_0^t l \frac{dt}{ql} \right).$$

Solving this equation, we get the current l as

$$l = l_0 \exp\left(-\mu_i Et/l\right) \tag{4}$$

where

$$l_0 = qn_0\mu_i E. \tag{5}$$

Thus, the initial gradient of log l vs t in Figure 5 at the first application of dc voltage in one direction may provide an information about ion mobility, μ_i, from

eq. (4). The ion density n_0 could be calculated from eq. (5) by using the current values at $t=0$ and the calculated mobility μ_i at each temperature. The obtained
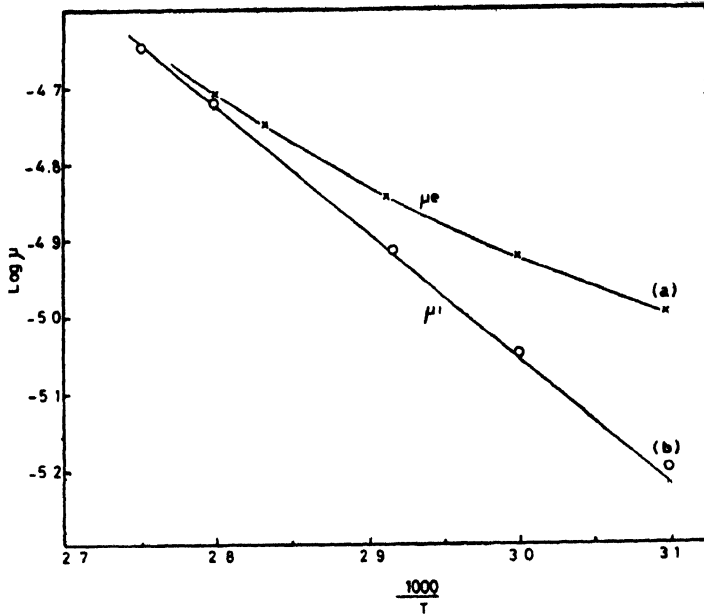

Figure 6. Log $\mu V_i 10^3/T$.

(a) μ_e calculated from eq. (3). (b) μ_i calculated from eq. (5).

mobilities μ_e and μ_i are plotted as a function of $10^3/T$ as shown in Figure 6. The values of μ_e and μ_i are fairly in good agreement above 70°C which might be due to the fact that the ion layer at low temperature is somewhat diffused one compared with that at higher temperature. The coincidence of μ_e and μ_i above 100°C had been observed by Kosaki et al (1970) in studying the electrical conduction of polyvinyl fluoride as stated above. The obtained values for μ_i, I_0 and n_0 are given in Table 2. It is clear that the ion density at zero time is equal to the ion

Table 2. The calculated mobility and ion density from the I-t slope and I at $t=0$.

$t°C$	I_0 at $t=0$ A	μ_i (cm^{2}v^{-1}s^{-1})	$n_0 = \frac{I_0}{q\mu_i E}$(cm^{-3})
50	3×10^{-5}	6.20×10^{-6}	2.5×10^{17}
60	9×10^{-5}	8.90×10^{-6}	5.3×10^{17}
70	4×10^{-4}	1.68×10^{-5}	1.2×10^{19}
80	2×10^{-3}	1.88×10^{-5}	5.6×10^{19}
90	10^{-3}	2.23×10^{-5}	2.3×10^{19}

density at current-peak and this supports the proposed mechanism for interpretation of the current hump.

References

Amborskl L 1962 *J. Polym. Sci.* **62** 331
Amin M, Sawaby A and Abd-Ghani S A 1980 *Egyptian J. Solids* **1** 271
Chutia J and Barva K 1980 *J. Phys.* **D13** 49
Ieda M, Kosaki M, Ohshima H and Shinohara U 1968 *J. Phys. Soc. Japan* **25** 1742
Ieda M and Shinohara U 1962 *Memoirs of the Faculty of Engineering, Nagoya University* **14** 150
Jain V K, Gupta C L and Jain R K 1978 *Ind. J. Pure Appl. Phys.* **16** 625
Jonscher A K 1967 *Thin Solid Film* **1** 213
Kadry N, Sawaby A, El-Agrami A and Sharkawi R 1984 *Isotopen Praxis.* **20** 312
Kamel R, Hilal M, Eid A H and Sawaby A 1975 *Mol. Cryst. Liq. Cryst.* **31** 9
Khera B, Sharma A K and Kaushik N K 1983 *Polyhedron* **2**(2) 108
Kosaki M, Ohshima H and Ieda M 1970 *J. Phys. Soc. Japan* **29** 1012
Lowis F H, Sutherland G 1948 *J. Org. Chem.* **13** 249
Molokhia N M 1986 *Acta Phys. Hung.* **60** 107
Munick R J 1956 *J. Appl. Phys.* **27** 1114
Nakajima T 1960 *Bull. Electrotech. Lab. Japan* **24** 801
Oster A 1967 *Z. Angew. Phys.* **23** 120
Rose A 1955 *Phys. Rev.* **97** 1538
Sahai R and Verma Rekha 1981 *J. Indian Chem. Soc.* **58** 640