

THE DIELECTRIC ABSORPTION PHENOMENA IN SODIUM ACETYLACETONATE COMPOUND

ABD EL-AZIM SAWABY, HASSEN H. AFIFY and ALI A. SHABAKA

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

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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—300 V 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 parameter including carrier mobility μ , mobile ion density n , activation energy of the conduction E_c and activation energy concerning the transport phenomenon E_μ .

1. Introduction

Although many investigations have been made on acetylacetonate as a good chelating agent and as solvent for electrochemistry measurements¹⁾, 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 studied²⁻⁶⁾. However, the available data is still far from being complete.

The present work 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.

2. Experimental technique

Sodium acetylacetonate compound was prepared by a conventional method⁷⁾. The purity of the sample was confirmed by different methods such as IR spectra and melting point. The sodium acetylacetonate powder was compressed at $2 \cdot 10^{10}$ Pa, in the form of discs (1.2 mm diameter and 1.7 mm thickness).

For electrical measurements, the disc was sandwiched 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 impedance 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 Fig. 1. The time dependence of current at voltage up to 5 ± 1 V could be negligible, but it becomes obvious at voltage above 8 V and their gradient tends to increase with voltage. The ten

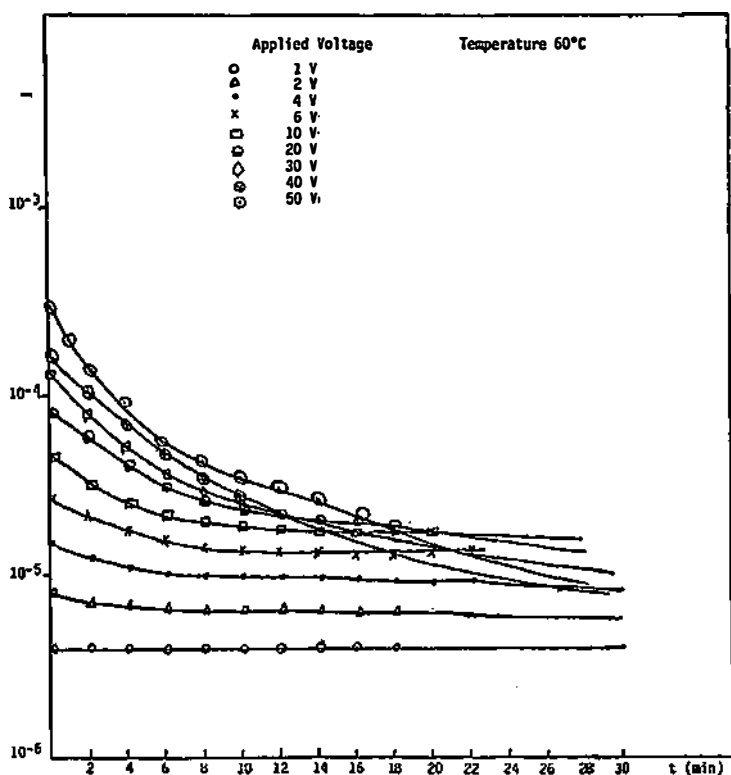


Fig. 1. $I-t$ relation at different voltage.

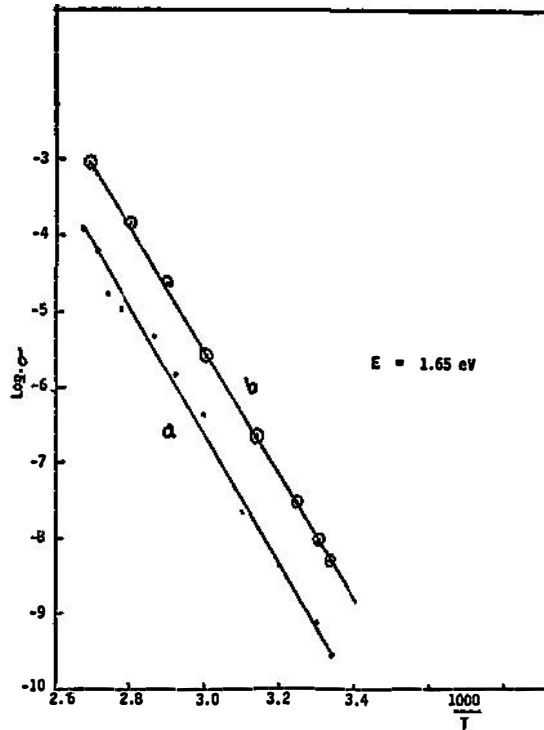


Fig. 4. $\log \sigma$ vs. $10^3/T$
 (a) two minutes after volt application
 (b) mean value of current before and after reversing the applied voltage.

TABLE 1.

I_{max}	temperature (°C)	t/s	$\mu = \frac{d^2}{tV}$ $cm^2 V^{-1} s^{-1}$	$n = \frac{I_{max}}{e\mu E}$
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	90	1.60×10^{-5}	3.0×10^{18}
6×10^{-3}	80	70	2.06×10^{-5}	1.6×10^{19}
6×10^{-2}	90	50	2.89×10^{-5}	1.1×10^{20}

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

cation of dc voltage on polymers, and therefore, $I-t$ curves in many cases change for a considerably long period⁸⁾. 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 °C⁹⁾. The first component of the absorption current is related to the relaxation process of dipole orientation in PVC¹⁰⁾.

On the contrary $I-t$ curves of the investigated samples shown in Fig. 2 appear to have an equilibrium leakage current at nearly room temperature and the time dependence of current becomes clearer as the temperature rises. Therefore, it could be assumed that the $I-t$ curves may be explained by the charge carrier beha-

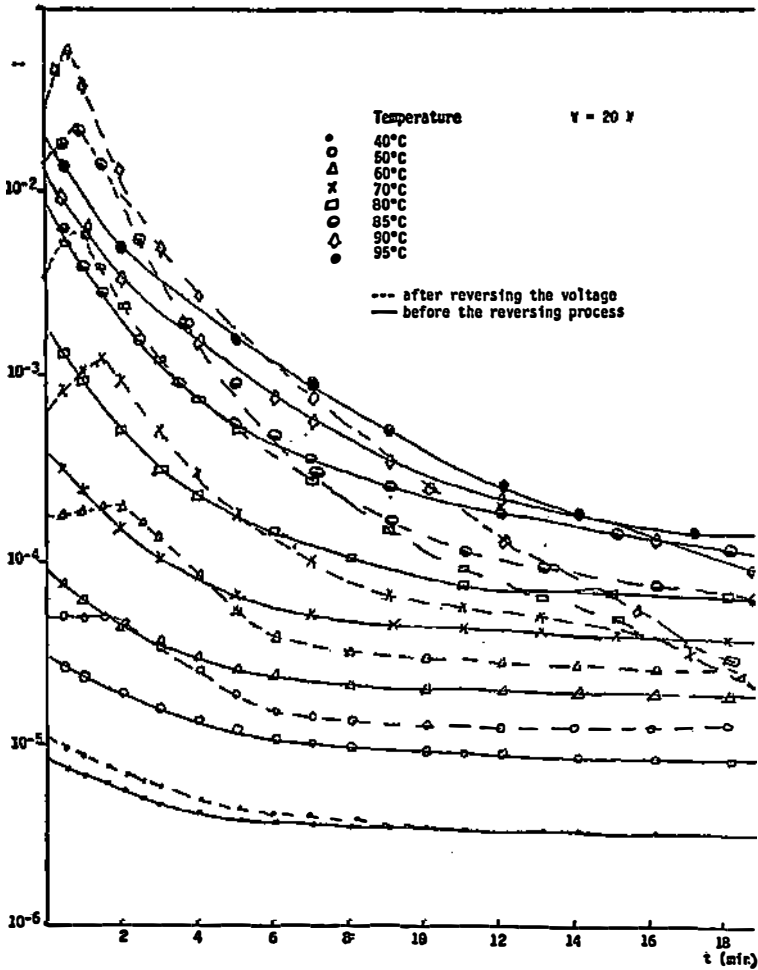


Fig. 5. $I-t$ relation before and after reversing the applied voltage.

viour. When a dc voltage is applied to the specimen an effective decrease of mobile ion density, which may be Na^{+11} , due to their arrival at the electrodes (clean-up) according to Faraday's law¹²⁾. Moreover, 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:

$$I(t) = qn\mu E^* \quad (1)$$

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 assists the explanation of current-time dependence. After the voltage application n and E^* are decreased with time due to space-charge effect which cause the current decrease with time. Thus the first component of $I-t$ curve in Fig. 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 well known relation:

$$\sigma = \sigma_0 \exp [\Delta E/kT]$$

with calculated $\Delta E = 1.65$ eV in the present work.

It is some times assumed as a general rule, the values for activation energies more than 0.6 or 0.8 eV would normally be associated with ionic transport, and values less than 0.2 eV could be considered as indicating undoubtedly electronic mechanism¹³⁾. Therefore, the obtained $\Delta E \cong 1.65$ eV for Na (ac, ac) may allow us to the infavour of ionic conduction mechanism. The deviation of $I-V$ curves from Ohm's law above 10 V may be due to an ionic layer build-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 of dc voltage in one direction. The $I-t$ curves given in Fig. 4 not only show the current peak clearance 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 insulation¹⁴⁾ and high plasticized PVC¹⁵⁾. The following mechanism could be used to explain the $I-t$ hump in Fig. 4. The fraction of the total ions arrived at each electrode may be accumulated there as immobilized ions without discharging at the electrodes. After the reversal of the applied voltage polarity, these ions may be mobile again. Therefore, the current may has its maximum when nearly all the immobilized ions are free to move in the specimen bulk. After an application of voltage for a certain periode (30 minutes in the present case) the ions are supposed to be accumulated in a thin layer near the electrode. Assuming that the number of ions released per unit time from this layer is proportional to the number of ions n remaining in the layer. Thus n changes with a rate:

$$dn/dt = -\gamma n, \quad n = n_0 \exp [-\gamma t] \quad (2)$$

where t is the time after the reversal of voltage polarity and n is equal to n_0 at $t = 0$. The transit time of ions between electrodes can be correlated to ion mobility by¹⁶⁾:

$$\mathcal{T} = l^2/\mu V \quad (3)$$

where l is the distance between electrodes (sample thickness), μ ion mobility and V is the applied voltage. Thus only as a first approximation disregarding the space charge effect \mathcal{F} might be correlated to t_{max} in $I-t$ curves in Fig. 5. Then equation (3) will be:

$$t_{max} \approx l^2/\mu V. \tag{4}$$

Hence, ion mobility μ_t could be estimated from t_{max} in equation (4) as well as ion density from I_{max} be using the equation $I = nq\mu E$. The calculated values for μ_t and ion density n together with I_{max} and t_{max} at each working temperature are given in Table 1. The ion density shows a thousand time increase in the temperature range 50–100 °C while the mobility has a slight increase.

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:

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

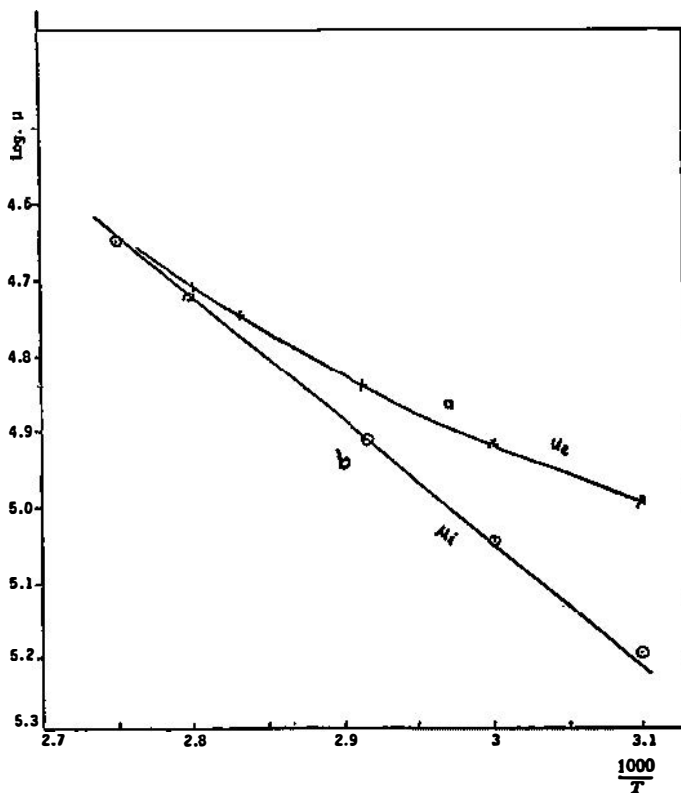


Fig. 6. $\log \mu$ vs. $10^3/T$
 (a) μ_e calculated from Eq. (3).
 (b) μ_t calculated from Eq. (5).

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 I at time t is given by:

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

Solving this equation, we get the current I :

$$I = I_0 \exp(-\mu Et/l) \quad (5)$$

where

$$I_0 = qn_0 \mu E. \quad (6)$$

Thus, the initial gradient of $\log I$ vs. t in Fig. 5 at the first application of dc voltage in one direction may provide an information about ion mobility, μ_j , from Eq. (5). The ion density n_0 could be calculated from Eq. (6) by using the current values at $t = 0$ and the calculated mobility μ_j at each temperature. The obtained mobilities μ_t and μ_j are plotted as a function of $10^3/T$ to calculate the activation energy as shown in Fig. 5. The values of μ_t and μ_j are fairly in good agreement each other above 70°C might be resulted from the fact that the ion layer at lower temperature is somewhat diffused one compared with that at higher temperature. The ion density at $t = 0$ has been calculated from Eq. (6) by substituting the calculated ion mobility μ_j from Eq. (5). The obtained values for μ_j , I_0 and n_0 are given

TABLE 2.

t °C	I_0 at $t = 0$	μ_t	$n_0 = \frac{e\mu_t E}{I_0}$
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^{18}
80	2×10^{-3}	1.88×10^{-5}	5.6×10^{18}
90	10^{-2}	2.23×10^{-5}	2.3×10^{19}

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

in Table 2. It is clear that the ion density at zero time is nearly equal to the ion density at current peak and this support the proposed mechanism for interpretation the current hump.

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DIELEKTRIČNI FENOMENI APSORPCIJE U SPOJEVIMA NATRIJ ACETILACETONATA

ABD-EL-AZIM SAWABY, HASSEN H. AFIFY i ALI A. SHABAKA

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

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Mjerena je električna vodljivost natrij acetilacetonata kao funkcija temperature, polja i vremena. $I-t$ karakteristika mjerena je u području napona 2—300 V i u temperaturnom intervalu 20—100 °C. $I-V$ karakteristika i dc vodljivost također je proučavana i diskutirana na bazi ionske vodljivosti.