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# SPLINE INTERPOLATION FOR TRAP SPECTROSCOPY ANALYSIS FOR TWO CYCLIC HYDROCARBONS

*Cubic spline interpolation gives a tool for obtaining good image of current-voltage characteristics for trap spectroscopy analysis without prior assumption about the trap distribution for 1-acenaphthenol and 9,10-dimethylanthracene.*

**Keywords**: 1-acenaphthenol, 9,10-dimethylanthracene, conductivity, electric characterization, trap spectroscopy, cubic spline.

## 1.  INTRODUCTION

Estimation of missing data in incomplete data base resulted either by a lack of physico-deterministic model of the phenomenon or use of uncertain data set as a batch for analysis needs efficient numeric algorithms. Complexity of the phenomena we ought to deal in the case of measurements for characterization of electrical properties force the use of special procedures for processing the measurements results. Thin layers of organic materials in the solid phase at room temperatures often exhibit a polycrystalline structure and polymorphism – which is favourable to the creation of additional trap levels, e.g. on grain boundary or on the voids, with previously undefined nature of energy distribution. In turn, the measurement itself can significantly modify the properties of material under study. This is due to the fact that the structural order developed in the course of preparing a layer may adopt more than one crystal structure ordering.

The temporarily resulted molecule coordination may be subject to the various compromises between close packing, hydrogen bonding, and $\pi$-$\pi$ stacking that can help in reveal in energetically feasible structures and the transition to the next state of equilibrium with a close energy that is just a few kJ/mol distant from the previous equilibrium may be very probable [1, 2]. Therefore, in the case of low melting organic materials the problem the investigator certainly meets is to ensure the stability of properties of the material under study. One of the solutions is aging measurement samples to ensure the stability of physical properties which are subject of the measurements. After the aging process, appearing e.g. as an annealing in the air or in the inert gas atmosphere or in the vacuum the resulted film properties may be significantly different from the corresponding properties shortly after formation of the layer.

Presented here measurements used biased voltages which polarized the layers with electric fields on the typical values of $E = 10^{-5} - 10^{7}$ V/m, which results in the additional structural changes and alterations of load state of the molecules forming a layer, what, as we have observed, is the reason for an additional dynamics of the changes of the measured values. A commonly known is the fact that the steady state current-voltage characteristics may significantly change their properties depending on whether the biasing voltage used for measurements was at increasing or at decreasing stage [3, 4]. There is no possibility to obtain a complete state of equilibrium due to slow relaxation processes in organic high resistant materials. Moreover, the current flow is associated with Joulle-Lenz heat dissipation, described with rule: $Q = UIt$ (where $U$ bias voltage, $I$ the current through the layer, $t$ – the time the current flown), what is an additional cause of deformation of the layer. Therefore, according to the current-voltage measurement when measurements are made at steady state the measurements should be carried out in a limited number of measuring points so as not to change the intrinsic properties of the layer. reducing the measuring step can only seemingly encourage increased measurement accuracy.

Used here trap spectroscopy methodology for developing experimental data requires stability layer properties in the course of measurement. Current stage of this methodology, which was used in the presented work, makes it possible to carry out calculations without *a priori* assumptions about the nature of the trap distribution as a function of energy. However, for extraction from the steady state current-voltage measurements informations on the interesting properties described quantitatively: such as free charge density – $n_f$, the total concentration of carriers (both free and trapped) – $n_s$, the density of states (DOS) distribution in respect to quasi-Fermi level ($E_F$) near the transport level – $h(E_F)$ or described qualitatively: such as unipolar o bipolar character of conduction for proper

biasing voltage *U*, there is requirement to obtain tabular dependence in the form allows the triple differentiation. The solution, adequate for trap spectroscopy, proposed by authors the works devoted steady state measurements is to use interpolation between measuring points which ensures a smooth derivative numerical methods [5, 6].

## 1.1. Cubic splines

Approximation of multiple nodes using the polynomial interpolation with polynomials of high degree takes into the problem of oscillation at the edges of an interval when the equispaced interpolation are used [7]. Higher degrees of polynomial interpolation do not always improve accuracy, moreover the task of interpolation polynomial of high level is also sensitive to disturbance of the data. The method allows to avoid this problem is to use spline functions (splines) with a smooth connections of the local polynomials, with initial condition of continuity for the first and second derivatives at the point of sticking polynomials. Analytical procedure leads to the formation of the tridiagonal matrix, that can be effectively solved by methods of elimination with simple algorithms [8]. Gerschgorin circle theorem [9] proves the uniqueness of the algorithm determining spline interpolation. Moreover, obtained shape of the function $y(x)$ satisfies the conditions of minimizing deformation energy described in the form of Euler-Lagrange equations [10].

## 1.2. Differential method for the space charge limited currents (DM-SCLC)

The evidence from the measurements of steady state current-voltage dependence is recognized in the tabular form of the functional relationship of the two column matrix, where the first column is destined for $U$ – values, understood as bias voltages, and the second one for $I$ – understood as values of the current flowing through the organic layer. After spline interpolation with the grid scale adequate for the later calculations, the determination procedure in the scope of the DM-SCLC can be made. As an input parameter for later analysis it is convenient to use the drift mobility taken from the volume of the layer, determined with use the methodology of transient currents generated with UV-light short pulse named as time of flight method (TOF). In the TOF there is not essential the presence of ohmic contacts between electrodes and measured layer [11, 12]. The requirement of the method of DM-SCLC is that the measuring cell for the measurements was in the form of a plane parallel sample with uniform dielectric layer between metal electrodes. Another assumption

being made for a method is constancy of the spatial distribution of the both density of traps and mobility within the layer. The calculations ignore the component of the diffusion current [13, 14]. The decisive for correctness of the trap spectroscopy calculations with use of DM-SCLC is possibility for determining smooth derivatives α, α' α'' calculated after the transformation of the $J - U$ (where $J$ is obtained after recalculation of the $I$ values to the $J = I/A$, where, $J$ – density of the current, $A$ – surface of the electrodes) to the double logarithmic scale, $\ln J - \ln U$

$$\alpha = \frac{d(\ln J)}{d(\ln U)} \quad \alpha' = \frac{d^2(\ln J)}{d(\ln U)^2} \quad \alpha'' = \frac{d^3(\ln J)}{d(\ln U)^3} \tag{1}$$

Calculations carried out on the basis of the method of DM-SCLC that are presented in this paper are referred to characterize the electrical properties of thin layers of two compounds 1-acenaphthenol and 9,10-dimethylanthracene. In previous papers [15, 16] concerning the characterization of the electrical properties of both above-mentioned materials the measurements of current-voltage dependence in steady state were subsequently interpreted quantitatively [15] using classical theory of SCLC currents for disordered materials [17, 18] and qualitatively [16] to determine the nature of carrier transport, using the elements of the theory of DM-SCLC [19, 20].

For the purposes of this work spline interpolations were performed by using the SRS1 program from the SRS1 Software LLC and the calculation of derivatives shown in formulas (1) and deconvolution to obtain the distribution of trap states as a function $h(E_F)$ were performed using Loger Pro Vernier Software & Technology program.

## 2.  EXPERIMENT

For the experiments were used commercially available 1-acenaphthol (1 ACOL) (purity 99%, Aldrich) and 9, 10-dimethylanthracene (9,10-DMA) (pure, Fluka). Test cells were made in the form of a planar capacitor with electrode area of 0.5 cm$^2$, where: the lower electrode – Au,  upper electrode – Al, the organic layer with a uniform thickness of 41 microns for 1 Acol, 18.5 microns for 9,10-DMA. All the layers forming the measuring cell were thermally deposited in vacuum of the order of $10^{-5}$ Tr. Measurements for current-voltage dependence were carried in the measurement system shown in Fig. 1, and the measurement procedure was in the manner described in detail in [16].
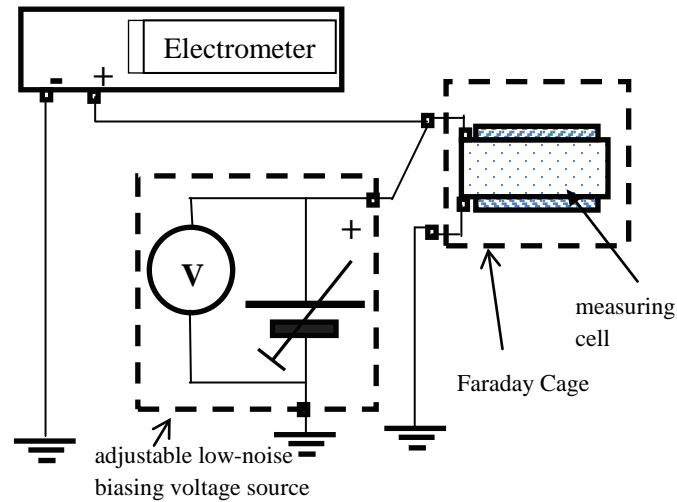
Fig. 1. Set-up for measurements of steady state current-voltage characteristics

The drift mobility value, $\mu_D$, were obtained by measurement performed by time of flight (TOF) in the measurement system such as that described in [21] (results not published). For 1-ACNOL the obtained value was $\mu_D = 1.1$ cm$^2$/Vs, for 9,10-DMA, $\mu_D = 0.14$ cm$^2$/Vs. These values were used to analyze the *J-U* characteristics obtained by the DM-SCLC. In Figure 2a) and b) are shown the obtained characteristics for both compounds under tests, presented on a log-log scale using only the points obtained during the tests. In Fig. 3a) and b) are shown the transformed characteristics $\alpha$ - *U* for both tested compounds by using only data points. Clearly visible is that to obtain higher-order derivative will lead to a violent jumping of the obtained dependence. In Fig. 4a) and b) are shown the transformed characteristics $\alpha$ - *U* for both tested compounds, but using the spline interpolation prior to calculation of the derivative characteristics. From above is obvious that the application of spline interpolation conduct to the possibility of obtaining a second ($\alpha'$) and a third derivative ($\alpha''$) having a form suitable for the calculation of DM-SCLC.
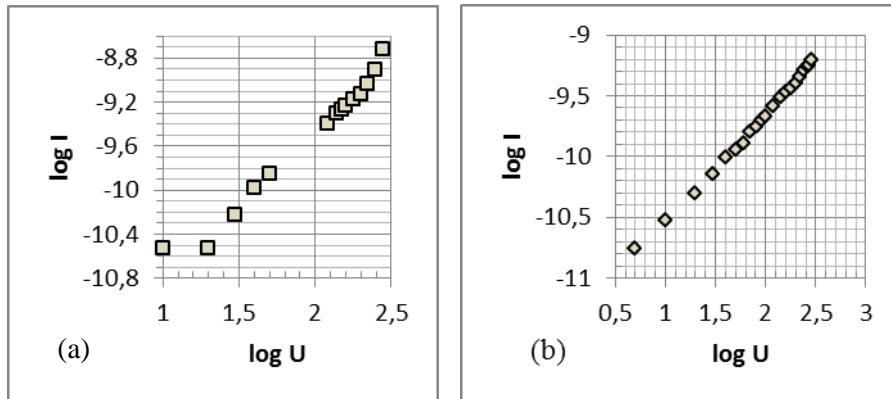
Fig. 2. Characteristics of *J* vs. *U* calculated for 1-ACNOL (L = 41 µm) a) and for 9,10-DMA (L = 18,5 µm) b), with use only the points obtained during the measuring tests
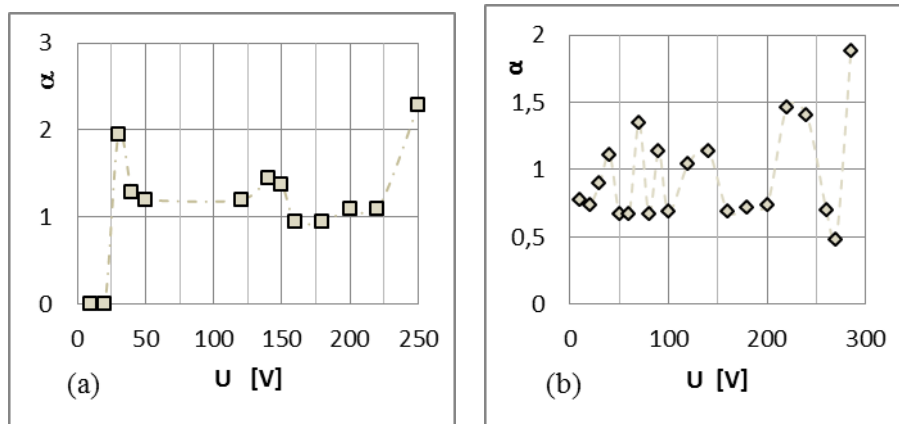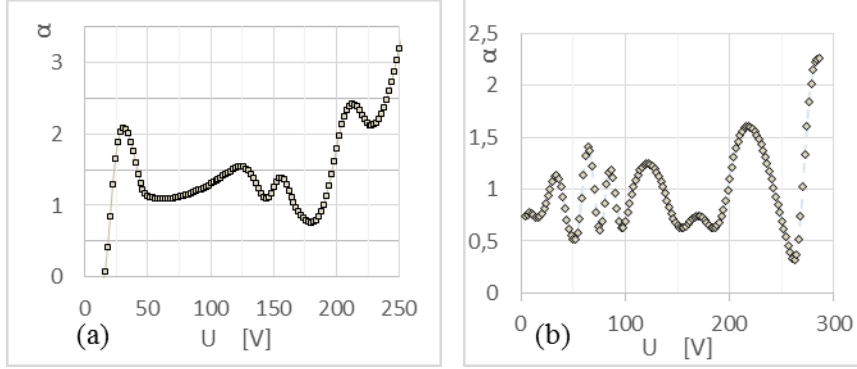


Fig. 3. Characteristics of $\alpha$ vs. *U* calculated for 1-ACNOL (L = 41 µm) a) and for 9,10-DMA (L = 18,5 µm) b), with use only the points obtained during the measuring tests

Fig. 4. Characteristics of $\alpha$ vs. $U$ calculated for 1-ACNOL (L = 41 µm) a) and for 9,10-DMA (L = 18,5 µm) b), with use the spline interpolation prior to calculation of the derivative characteristics

## 2.1. Trap spectroscopy with use of spline interpolation for DM-SCLC

The analysis of the obtained experimental evidence in the scope of trap spectroscopy for calculation of presented here quantities use the set of the equations [5, 6, 15, 16, 22, 23, 24]

$$n_{fL} = \frac{\alpha}{2\alpha - 1} \frac{JL}{e\mu U} \tag{2}$$

$$n_{sL} = \frac{\rho_L}{e} = \frac{2\alpha - 1}{\alpha} \frac{\alpha - 1}{\alpha} \left[1 - \frac{\alpha'}{\alpha(2\alpha - 1)(\alpha - 1)}\right] \frac{\varepsilon\varepsilon_0 U}{eL^2} \tag{3}$$

$$E_F = kT \ln\left(\frac{N_{cv} e\mu}{L}\right) + kT \ln\left(\frac{J}{U}\right) + kT \ln\left(\frac{\alpha}{2\alpha - 1}\right) \tag{4}$$

where $e$ is the electron charge; µ is the drift mobility of charge carriers (in this paper taken from TOF measurements); $L$ is the sample thickness; $\varepsilon_0$ is dielectric constant; $\varepsilon$ is the dielectric permittivity of the material; $n_{fL}$ is the concentration of free charge carriers at the cathode (later the index $L$ in the subscript will be not used); $n_{sL}$ is the actual concentration of carriers captured by local states near cathode; $\rho_L$ is the space charge density limiting the current; $E_F$ – position of quasi Fermi level, $k$ is the Boltzmann constant, $T$ is temperature, $N_{cv}$ is effective density of states in the transport level.

The distribution function of local state density at high temperature approximation can found by the convolution

$$\frac{dn_s}{dE_F} = \int\limits_E h(E) \frac{df(E - E_F)}{d(E - E_F)} dE \tag{5}$$

where $f(E - E_F)$ is the Fermi-Dirac function.

In Fig. 5, 6 and 7 we can see the power of the DM-SCLC spectroscopy. The microscopic parameters of the organic layer can be recognized from macroscopic measurements, in the manner of simple steady state current-voltage dependence.

Clearly seen is the resolving power of the trap spectroscopy, for both tested materials the same physical quantities take the different values, differ in several orders of magnitude for $n_f$ and different in the case of total density of charge $n_s$ and the distribution of local states (density of traps).
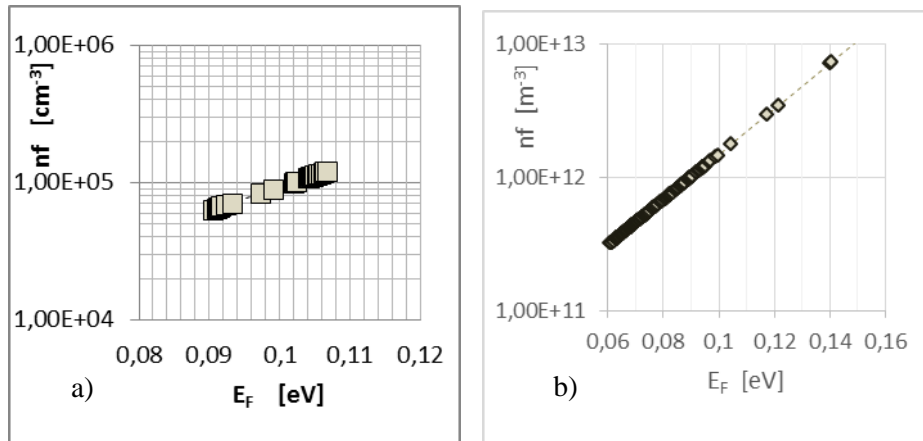


Fig. 5. Characteristics of $n_f$ vs. $E_F$ calculated for 1-ACNOL (L = 41 µm) a) and for 9,10-DMA (L = 18,5 µm) b), with use the spline interpolation prior to calculation of the derivative characteristics

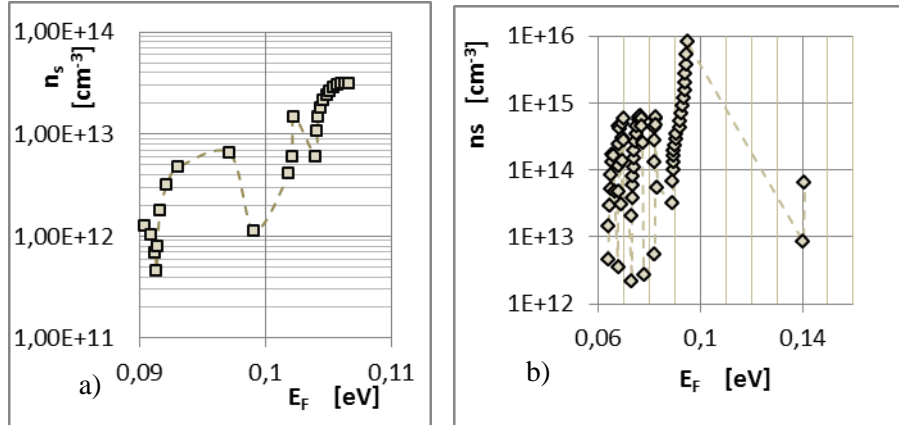Fig. 6. Characteristics of $n_s$ vs. $E_F$ calculated for 1-ACNOL (L = 41 µm) a) and for 9,10-DMA (L = 18,5 µm) b), with use the spline interpolation prior to calculation of the derivative characteristics



Fig. 7. Characteristics of $n_s$ vs. $E_F$ calculated for 1-ACNOL (L = 41 µm) a) and for 9,10-DMA (L = 18,5 µm) b), with use the spline interpolation prior to calculation of the derivative characteristics
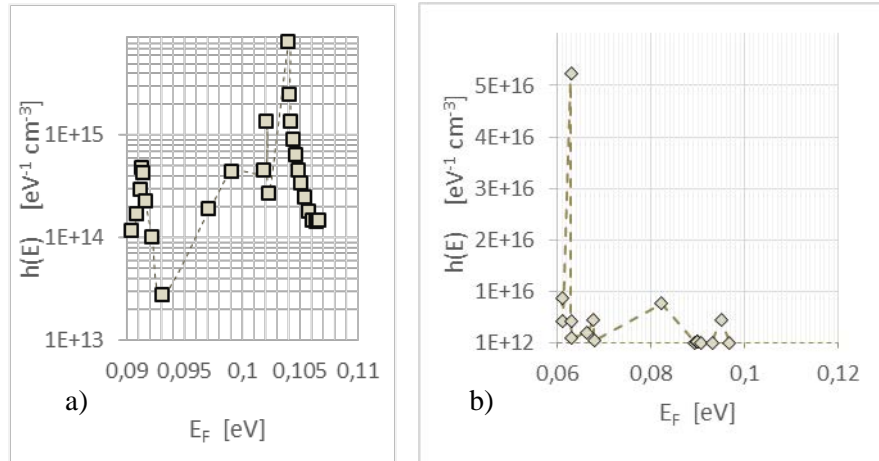
The analysis of trap density (from Fig. 7) made with numeric integration gives a total density of traps for 1-ACNOL, $N_t = 5.75 \cdot 10^{18}$ cm$^{-3}$ (the mean distance between traps 5,6 nm), and for 9,10-DMA, $N_t = 1.55 \cdot 10^{14}$ cm$^{-3}$ (the mean distance between traps 186 nm).

## 3. CONCLUSIONS

Trap spectroscopy applied without prior assumptions about the shape of the local density of states the in the scope of presented here paper shows his advantages in fast calculations for quantities describing microscopic conditions of the carrier transport.

In the case of low molecular weight organic materials spline interpolation allows to transform the simply current – voltage steady state tabular dependence into dependencies usable for trap spectroscopy, which require calculation of first, second and third derivatives of the J-U dependence in log - log scale.

The knowledge obtained with use of DM-SCLC trap spectroscopy can be used for determination of the proper work conditions for the electronic devices based on materials tested.

## Acknowledgements

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# INTERPOLACJA Z UŻYCIEM SPLAJNÓW W ZASTOSOWANIU DO SPEKTROSKOPII PUŁAPEK DLA ANALIZY DWU CYKLICZNYCH WĘGLOWODORÓW

## Streszczenie

Interpolacja z wykorzystaniem splinów sześciennych daje dobre narzędzie dla uzyskiwania dobrych obrazów charakterystyk prądowo-napięciowych dla celów spektroskopii pułapkowej prowadzonej bez uprzedniego założenia o rozkładzie pułapek dla 1-acenaftenolu i 9,10-dimetyloantracenu.