Charge Transport in Organic Photoreceptors: What Theory Tells Us About Interpretation of Experimental Data

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Abstract

We present analysis of the mobility field dependence in disordered organic materials for the model of mixed dipolar-quadrupolar disorder. The analysis shows that the reliable separation of contributions from the different sources of disorder could be achieved only in rare cases. Additionally, we discuss the unusual dependence of the charge carrier drift mobility in molecularly doped polymers on the concentration of traps which has been observed recently. This dependence differs from the expected inverse proportionality that should be valid for trap-controlled transport. Using simulation results we argue that reason for this dependence is the faulty method of the mobility calculation from photocurrent transient. Our results also show that the mobility, estimated from the time of intersection of the asymptotes to plateau and trailing edge of photocurrent transient, is very sensitive to variation of transient shape and, in some cases, effectively masquerades real concentration and field dependence of the true mobility.

Introduction

Recent years significantly changed our understanding of the charge carrier transport in disordered organic materials. We understand now that the main property that governs the transport behavior of the materials is the spatial correlation in the distribution of the energy levels of transport sites.[1-5] For example, the spatial correlation is responsible for the Poole-Frenkel (PF) dependence of the carrier drift mobility on the electric field that is generally observed in polar disordered organic materials

$$\mu \propto \exp\left(\gamma\sqrt{E}\right). \qquad (1)$$

At the same time, this new approach made more complicated the analysis of the experimental data in order to obtain the relevant parameters which describe properties of the particular material. We should mention here that the older Gaussian disorder model (GDM)[6] popularized too simplistic approach to the analysis of experimental data. Indeed, in this model

$$\mu = \mu_0 \exp\left(-(2\sigma/3kT)^2 + C\left[(\sigma/kT)^2 - \Sigma^2\right]\sqrt{E}\right), \qquad (2)$$

where σ is the width of the total density of state (DOS), $C \approx 2.9 \times 10^{-4}$ (cm/V)$^{1/2}$, and Σ is the parameter that characterizes the spatial disorder. So, to characterize any material, you just need to know three parameters μ_0, σ, and Σ. More important, the most significant parameters σ and Σ describe the contributions from all types of disorder in the uniform way that does not depend on the particular kind of disorder. Hence, in the GDM different kinds of disorder (disorders of different nature) are indistinguishable. Recent results show that this is not true.[3,7]

Could We Separate Contributions From Different Kinds Of Disorder?

To discuss the situation in more detail we limit our consideration to the 1D model of charge carrier transport where carrier motion in 3D medium is limited to the straight line oriented along the field direction. In this model[3]

$$\mu = \frac{\mu_0 kT}{eE\int_0^\infty dy \exp\left(-eyE/kT + [C(0)-C(y)]/(kT)^2\right)} \qquad (3)$$

and the mobility field and temperature dependence is determined by the spatial behavior of the binary energy-energy correlation function

$$C(\mathbf{r}) = \left\langle U(\mathbf{r})U(0)\right\rangle. \qquad (4)$$

Extensive Monte Carlo simulation of the transport in 3D dipolar medium showed that the 1D model gives a reasonably good description of charge carrier transport.[5] In a typical case site energy U(r) contains contributions Ui(r) from different sources of disorder (dipolar, quadrupolar, non-correlated, and so on.[3,7]). Assuming for simplicity reason that different kinds of disorder give totally noncorrelated contributions, we can write the correlation function C(r) as a sum of individual contributions

$$C(\mathbf{r}) = \sum_i C_i(\mathbf{r}), \ C_i(\mathbf{r}) = \left\langle U_i(\mathbf{r})U_i(0)\right\rangle. \qquad (5)$$

Different terms in (5) have, in general case, different dependences on **r**,[1,3,7] and, thus, different kinds of disorder do differ from each other. For example, for the dipolar disorder[1,3]

$$C_d(\mathbf{r}) = 0.74\sigma_d^2 \frac{a}{r} \ , \tag{6}$$

while for quadrupolar disorder[7]

$$C_q(\mathbf{r}) = 0.5\sigma_q^2 \left(\frac{a}{r}\right)^3 \tag{7}$$

(here a is the minimal separation between charge carrier and dipolar or quadrupolar molecule). Correspondingly, the resulting mobility field and temperature dependence is not the same for different kinds of disorder. For example, in the case of pure dipolar disorder[3]

$$\ln \mu \propto -\left(\frac{\sigma_d}{kT}\right)^2 + 2\frac{\sigma_d}{kT}\sqrt{eaE / kT} \ , \tag{8}$$

while for pure quadrupolar disorder[7]

$$\ln \mu \propto -\left(\frac{\sigma_q}{kT}\right)^2 + \frac{2^{3/2}}{3^{1/4}}\left(\frac{\sigma_q}{kT}\right)^{1/2}\left(eaE / kT\right)^{3/4} . \tag{9}$$

Mobility field dependence for the mixture of dipolar and quadrupolar disorder and Miller-Abrahams hopping rate is presented in Figure 1. Contribution from the Van der Waals component gives mobility field dependence ln$\mu \propto E^{5/6}$ and for the trap-controlled transport ln$\mu \propto E$. Note, that the quadrupolar mobility field dependence (9) should be quite common in weakly polar organic disorder materials,[7] and mixture of dipolar and quadrupolar disorders should be a good model for the general case of trap-free disordered organic material.

It follows from (3-5) that in general case, if we have contributions from several kinds of disorder with comparable values of σ_i, then it is not possible to present a simple formula for the mobility field and temperature dependence that could be comparable with (2). Figure 1 obviously confirms this statement. With the decrease of the dipolar contribution the mobility field dependence gradually transforms from the dependence (8) to the dependence (9).

However, mobility field dependence could present a clear indication of the existence of several contributions to (5) only when mobility is measured in exceptionally wide field range (in Figure 1 field changes by more than 3 orders of magnitude). Taking into account a limited field range accessible in real experiments, quite poor accuracy of experimental data, and inevitable contribution of dispersive transport (which brings the quadrupole dependence (9) even more close to the PF dependence (8) [7]), the possibility to calculate individual contributions σ_i from experimental data seems to be dubious.

Quite frequently the field range analyzed in experiments is about one order of magnitude (or even more narrow), and in this limited range the field dependence (9) is not clearly distinguishable from the dependence (8). In this case an experimental mobility field dependence looks quite linear when plotted as lnμ vs $E^{1/2}$, but an attempt to analyze it in terms of dipolar model (8) would result in meaningless value for σ_d. The same arguments are valid for the analysis of the mobility temperature dependence. We should admit that the reliable separation of different contributions to the total DOS width σ could be achieved only in rare cases.

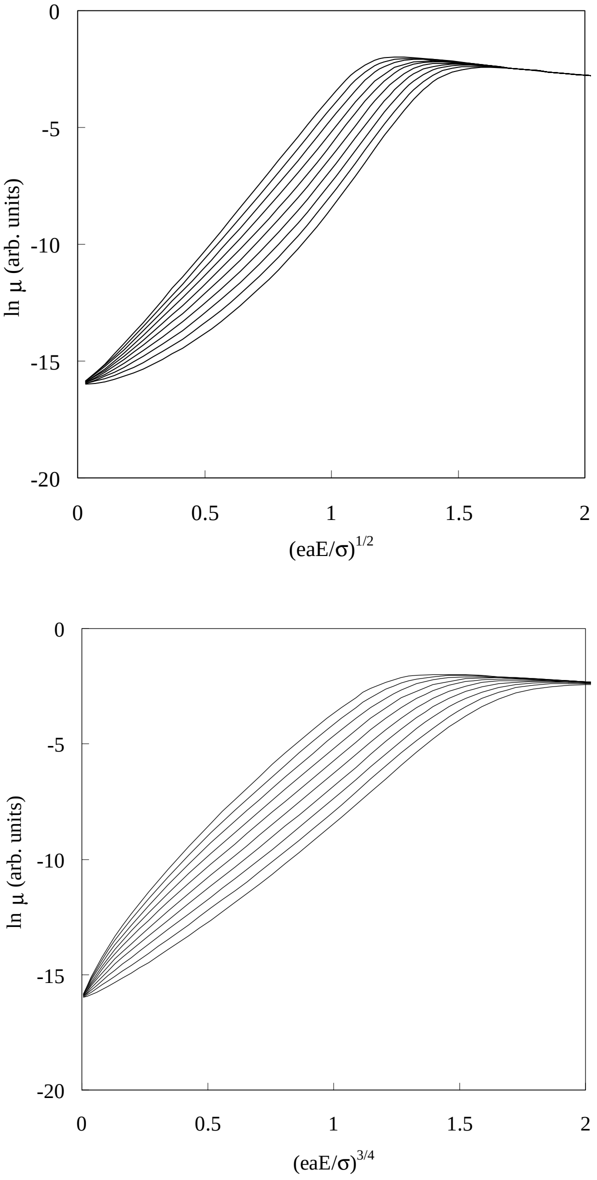

Figure 1. Mobility field dependence for the mixture of dipolar and quadrupolar disorders with σ_q / σ_d *varied from 0 to 1 (step 0.1, from the top curve downwards) and kT/σ =0.25, where* $\sigma^2 = \sigma_d^2 + \sigma_q^2$ *. If σ = 0.1 eV and a = 10A, then eaE/σ ≈ 1 at E = 106 V/cm.*

How to Calculate the Carrier Drift Mobility from the Photocurrent Transient

For the calculation of the carrier drift mobility from the experimentally measured photocurrent transient two different procedures are generally used. In the first one, the mobility value is calculated from the time of intersection of two asymptotes - to the plateau and to the trailing edge of the transient (μ_i); in the second procedure the time for photocurrent to decay to the half of its plateau value I_p is used ($\mu_{1/2}$, see Figure 2). The first method is the method of choice for most experimental papers. There is a generally accepted opinion that in the case of essentially nondispersive transport it is not important which method is used for the mobility calculation: field and temperature dependences of mobilities, calculated by different methods, are essentially the same apart from insignificant difference in mobility value. We are going to demonstrate that this is not true at least in the case of trap-controlled charge transport in disordered dipolar materials.

Our previous results[7] indicate that the PF dependence for dipolar materials in moderate fields remains essentially the same in the presence of traps (apart from the trivial vertical displacement of the curve downwards) *for any trap concentration and depth*, while in stronger fields a new dependence develops, namely the linear one

$$\ln \mu \propto eaE / kT \qquad (10)$$

where a is close to the mean distance between transport sites.

In recent papers Vertas and Juhas,[8] Wolf et al.[9] and Lin et al.[10] studied the transport of holes in doubly doped polymer layers. Molecules of one dopant, added in small concentration, and possessing significantly lower ionization potential, served as traps for charge carriers. In these studies it was found that, for shallow traps, the PF dependence remains mainly untouched[8,10] while for deep traps a linear dependence (10) was observed *in the whole field range.*[8] This result is in striking disagreement with the predictions of the theory.[7]

The most puzzling experimental result, first observed in [8] and later confirmed in [10], is the unusual dependence of the mobility on trap concentration c

$$\mu \propto 1 / c^n \qquad (11)$$

with $n > 1$ instead of expected dependence with $n = 1$ for trap-controlled transport. This result does not agree with the theoretical dependence found in [7], where $n = 1$.

Results of computer simulation (details of simulation are described in [5,7]) of hopping transport in 3D dipolar medium containing traps show that the sole reason for these discrepancies with theoretical results is the particular method of the mobility calculation (intersection method), used in [8,10]. This method overestimate the contribution of fast carriers and in some cases effectively masquerades the real mobility dependence on E and c. Figures 3 and 4 show that the mobility, calculated by the one-half procedure, much better agrees with mobility calculated from the mean carrier velocity $\langle v \rangle$.

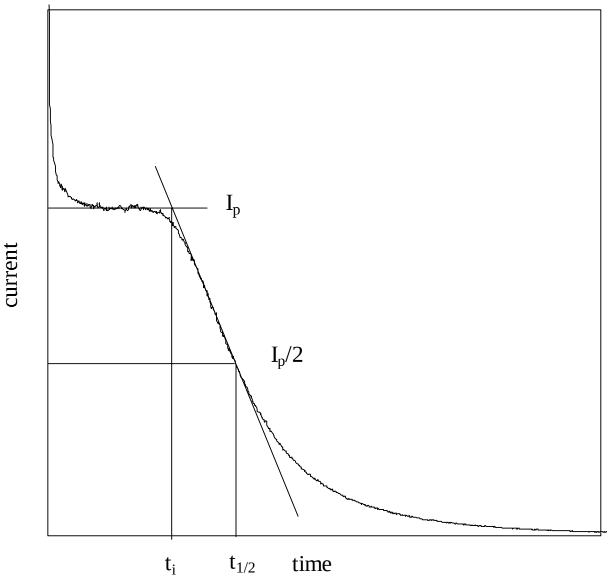

Figure 2. Two methods of mobility calculation from the experimentally measured transient: $\mu_i = L/t_i E$ and $\mu_{1/2} = L/t_{1/2} E$, here L is the sample thickness.

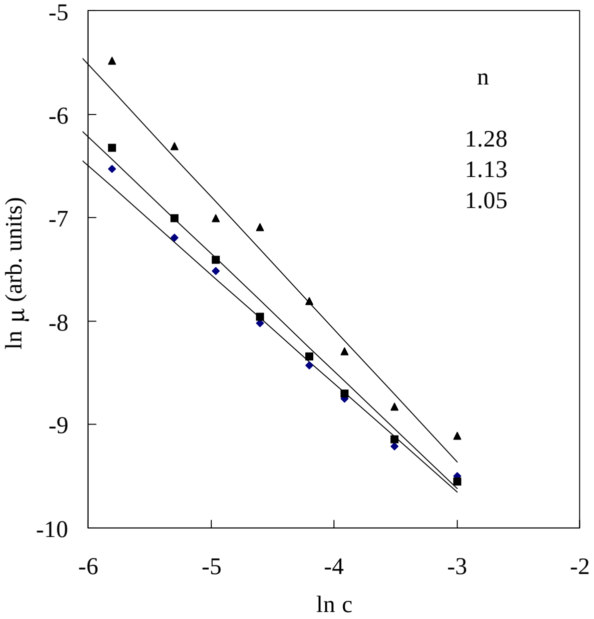

Figure 3. Mobility dependence on the trap concentration for $\sigma/kT = 3.83$, $eaE/\sigma = 0.44$, $\Delta/kT = 10$, and $L = 1{,}000{,}000$ lattice planes for different methods of mobility calculation: $\mu_v = \langle v \rangle / E$ - diamonds ($n = 1.05$), $\mu_{1/2}$ - squares ($n = 1.13$), and μ_i - triangles ($n = 1.28$). Here Δ is trap depth. If $T = 298$ K and $a = 10$ A, then $\sigma = 0.098$ eV, $E = 4.3 \times 10^5$ V/cm, and $\Delta = 0.26$ eV.

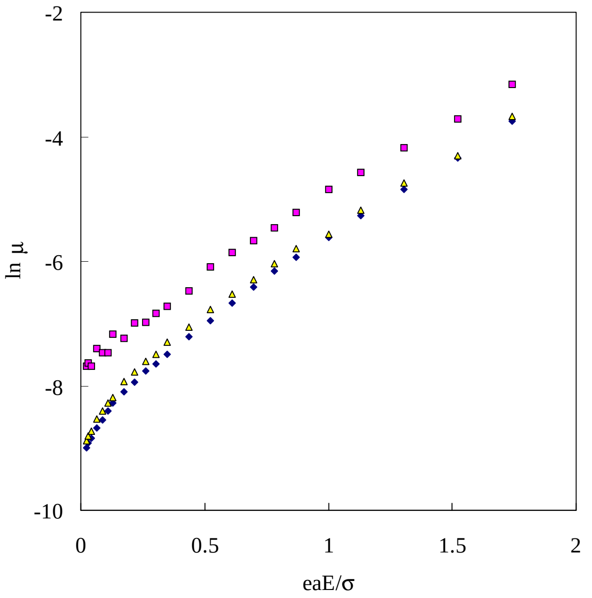

Figure 4. Mobility dependence on the electric field for σ/kT = 3.83, Δ/kT = 10, c = 0.01, and L = 40,000 lattice planes for different methods of mobility calculation: μ_v *- diamonds,* $\mu_{1/2}$ *- triangles, and* μ_i *- squares.*

At last we would like to note that the best way to calculate the mobility (from the point of view of its closeness to the usual definition as the mean carrier velocity over the electric field strength) is to use the formula

$$\mu = \frac{\langle v \rangle}{E} \approx \frac{I_p L}{EQ} = \frac{I_p L}{E\int_0^\infty dt I(t)} \qquad (12)$$

where Q is the total charge flowed through a sample. This formula can be used when a real plateau with an approximately constant current $I(t) \approx I_p = e\rho \langle v \rangle S$ is detected (here ρ is the density of carriers and S is the sample area), and one can measure the photocurrent for a long time interval, sufficient to calculate Q with good accuracy.

Conclusion

We analyzed the mobility field dependence for the most realistic case of the mixture of dipolar and quadrupolar disorders. Our results indicate that the reliable separation of the contributions from different kinds of disorder may be achieved only in rare cases, when it is possible to measure a nondispersive mobility in broad field range.

We showed that in some situations the mobility, calculated in a usual way, by the time of intersection of two asymptotes - to the plateau region and to the trailing edge of the transient, plays a misleading role in the revelation of the mobility dependence on the electric field and trap concentration. The best way to calculate the nondispersive mobility is to use Eq. (12). If it is not possible for some reason, then the mobility, calculated by the time for photocurrent to decay to the half of its plateau value, should be used for discussion of experimental results.

Acknowledgments

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References

1. S. V. Novikov and A. V. Vannikov, *J. Phys. Chem.*, **99**, 14573 (1995).
2. Yu. N. Gartstein and E. M. Conwell, *Chem. Phys. Lett.*, **245**, 351 (1995)
3. D. H. Dunlap, P. E. Parris, and V. M. Kenkre, *Phys. Rev. Lett.*, **77**, 542 (1996).
4. S. V. Novikov, A. V. Vannikov, *Proc. SPIE*, **2850**, 130 (1996).
5. S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, and A. V. Vannikov, *Phys. Rev. Lett.*, **81**, 1472 (1998).
6. H. Bässler, *Phys. Status Solidi B*, **175**, 15 (1993).
7. S. V. Novikov, D. H. Dunlap, and V. M. Kenkre, *Proc. SPIE*, **3471**, 181 (1998).
8. J. Veres and C. Juhasz, *Phil. Mag. B*, **75,** 377 (1997).
9. U. Wolf, H. Bässler, P. M. Borsenberger and W. T. Gruenbaum, *Chem. Phys*., **222,** 259 (1997).
10. L. B. Lin, P. M. Borsenberger, E. H. Magin, S. A. Visser, and W. T. Gruenbaum, *Proc. SPIE*, **3471,** 174 (1998).