

An Unusual Dependence of the Charge Carrier Mobility in Disordered Organic Materials on Trap Concentration: Real Phenomenon or Artifact?

S. V. Novikov

A.N. Frumkin Institute of Electrochemistry, Moscow, Russia

Recently an unusual dependence of the charge carrier drift mobility in molecularly doped polymers on the concentration of traps has been reported. This dependence differs from the expected inverse proportionality that should be valid for trap-controlled transport. Using the results of computer simulation we argue that the reason for this dependence is different regimes of charge carrier transport for layers with different trap concentrations, i.e., dispersive transport for small trap concentrations and nondispersive transport for high trap concentrations. Our results also show that mobility, as estimated from the time of intersection of the asymptotes to the plateau and trailing edge of the photocurrent transient, is very sensitive to variations of its shape and, in some cases, effectively masks the real concentration and field dependence of the true mobility.

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Introduction

Charge transport in molecularly doped polymers^{1,2} (MDPs) is of significant interest because of its importance in the xerographic process where MDPs serve as transport layers in dual-layer photoreceptors. Knowledge of the transport properties of these materials is an essential part of the technological know-how for design of high-speed laser printers and copiers. At the same time, MDPs are members of a broad class of organic disordered materials with common transport features. Other examples of materials of this class are low molecular weight organic glasses^{3,4} and certain conjugated polymers.^{5,6} Recent efforts^{7–14} have established a new basis for understanding the transport properties of these materials. It has been found that the most fundamental property of charge transport, the so-called Poole-Frenkel (PF) mobility field dependence^{1,2,5}

$$\mu \propto \exp(\gamma\sqrt{E}) \quad (1)$$

arises naturally in disordered dipolar systems where a carrier's interaction with randomly oriented and situated molecules possessing permanent dipole moments provides a significant contribution U_d to the total site energy. The most important property of a dipolar medium is the strong spatial correlation in the distribution of energies of transport sites (σ) that can be characterized by slow decay of the corresponding correlation function

$$C(r) = \langle U_d(r)U_d(0) \rangle \propto \sigma^2 \frac{a}{r} \quad (2)$$

where $\sigma^2 = \langle U_d^2 \rangle$, and a is a minimal charge-dipole separation.^{7,9} In recent studies^{7,9,10,14} it has been shown that the model of dipolar glass gives a good explanation of the main transport properties of disordered organic materials. Extensive computer simulations suggest that the overall mobility dependence on electric field and temperature in correlated (dipolar) media has the form¹⁴

$$\mu = \mu_0 \exp \left[- \left(\frac{3\hat{\sigma}}{5} \right)^2 + C_0 (\hat{\sigma}^{3/2} - \Gamma) \sqrt{\frac{eaE}{\sigma}} \right], \quad (3)$$

where $\hat{\sigma} = \sigma/kT$, $C_0 = 0.78$, and parameter Γ equals to 2 for dipolar glass with no positional disorder but should be greater for spatially disordered system. Analytic solution of the 1D version of dipolar model shows⁹ that PF mobility dependence is a direct consequence of the particular asymptotic decay of correlation function (Eq. 2).

In recent studies, Vertas and Juhas,¹⁵ Wolf and co-workers,¹⁶ and Lin and co-workers¹⁷ studied the transport of holes in doubly doped polymer layers. Molecules of one dopant, added in small concentration, and possessing significantly lower ionization potential, serve as traps for charge carriers. In these studies it has been found that for shallow traps the PF dependence remains mainly untouched,^{15,16} while for deep traps a different type of mobility field dependence was observed, namely

$$\ln \mu \propto eaE/kT \quad (4)$$

where a is close to the mean distance between transport sites.¹⁵

In our study,¹³ the trap-affected transport in dipolar glasses has been studied using computer simulation as

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well as an exact analytic solution of the 1D model. The main result is that the addition of traps (no matter how deep) does not destroy the PF field dependence in weak fields, though it produces linear dependence (Eq. 4) for stronger fields. This result is valid both for 3D and 1D dipolar glasses and seems to be in direct contradiction with the result of Ref. 15, where for deep traps the linear dependence (Eq. 4) was observed in the whole field range, starting from very small fields. This discrepancy will be addressed in more detail later.

The most puzzling experimental result, first observed in Ref. 15, and later confirmed in Ref. 17, is the unusual dependence of the mobility on trap concentration c

$$\mu \propto 1/c^n, \quad (5)$$

with $n > 1$ instead of the expected dependence with $n = 1$ for trap-controlled transport. This result does not agree with the theoretical dependence found in Ref. 13, where $n = 1$. Resolution of this disagreement is the main purpose of this study.

In Ref. 15 it was found that for two particular kinds of traps $n \approx 1.33$, while in Ref. 17 several different traps were investigated and it was found that n is a monotonously increasing function of trap depth with $n > 1$ for deep traps ($\Delta > 0.22$ eV, where Δ is a trap depth). Note, that Eq. 5 with $n = 1$ is a common feature of the trap-controlled transport regime for any reasonable model of hopping charge transport and small trap concentration (when we can neglect the direct hops between traps). Indeed, this dependence means that at small concentrations, traps act independently and do not notably alter the transport properties of the surrounding matrix. Thus, the solution of this puzzling concentration dependence seems to be of significant interest for a general understanding of the properties of hopping transport.

Unusual Concentration Dependence as a Result of Dispersive Effects. The first clue for the solution of the concentration puzzle is the obvious difference in the characteristics of the photocurrent transients for different concentrations of traps. Namely, at room temperature the transient for the trap-free matrix usually has a nondispersive shape: a short initial spike, then a well-defined plateau, and then an abrupt decrease (see Fig. 1 for $c = 0$). Such a shape indicates that the major part of the carriers moves with approximately uniform velocity. After the addition of a small quantity of traps, the photocurrent transient exhibits dispersive features (in some cases the transient becomes so dispersive that even determination of the drift time in a double linear plot is not possible). For greater trap concentrations, the transient again becomes nondispersive with much lower mobility (in comparison to the trap-free case). At last, for a significant concentrations of traps, the mobility increases because direct hopping between traps becomes possible: this regime is of no interest for the trap-related problem. The transition from nondispersive trap-free transport to nondispersive trap-controlled transport is shown in Fig. 1. This figure is the result of computer simulation but demonstrates the same type of behavior as the experimental data in Ref. 15.

Hence, in a typical experimental situation, for a relatively thin transport layer, the mobility at different trap concentrations is measured in very different transport regimes: dispersive transport for small trap concentrations and nondispersive for high trap concentrations (see, for example, Fig. 3 in Ref. 15). For the same value of temperature and electric field the dispersive mobility is

greater than the nondispersive equilibrium mobility (supposing we can measure both of them, for example, in layers of different thickness). Dispersive mobility is greater because this is the mobility of hot carriers which do not undergo full energy relaxation. Hence, the true nondispersive mobility for small trap concentrations (measured in very thick layers) should be smaller than the mobility measured in Refs. 15, 17. Figure 2 demonstrates that this modification should lead to a decrease of n ; it is possible that in such a case $n = 1$, as it should be for trap-controlled transport.

Computer Simulation

To test this explanation we carried out computer simulations of trap-affected charge carrier transport in disordered organic materials of dipolar origin. For the transport simulation we used a simple cubic lattice of $50 \times 50 \times 50$ sites with lattice parameter a , occupied by randomly oriented dipoles with dipole moment p , from which an extended transport layer is formed by periodic continuation. The energy of a carrier at a given site is then the sum (calculated using the Ewald method¹⁸) of its interaction with dipoles at all sites except its own. For this particular model of a dipolar glass^{19,20}

$$\sigma = 2.35 ep/\epsilon a^2, \quad (6)$$

where ϵ is the dielectric constant. For a fraction c of all transport sites, a constant value Δ was subtracted from the site energy, thus modeling traps of all transport sites.

To determine the photocurrent transients, we have performed Monte Carlo (MC) simulations using the Miller-Abrahams hopping rate that falls off with distance as $\exp(-2\alpha r)$. We take $2\alpha = 10$, as in Ref. 21. At each particular time the current was calculated as a quantity, proportional to the instantaneous velocity of charge carrier. To save computation time, for each transport site we only consider hops to all other transport sites that occur with probability greater or equal to 10^{-5} of the maximum probability for this particular site.

We calculated mobility using three different methods: (1) $\mu_v = \langle v \rangle / E = L \langle 1/t_{MC} \rangle / E$, where $\langle v \rangle$ is the average velocity of a carrier, L is the layer thickness, and t_{MC} is the time that a carrier needs to reach the opposite electrode; unfortunately, one cannot calculate μ_v directly from the temporal dependence of the photocurrent, hence, this method, being the superior one from the theoretical point of view, cannot be applied to analysis of experimental data; (2) $\mu_i = L/t_i E$, where t_i is the time of intersection of the asymptotes to the plateau and trailing edge of the transient; (3) $\mu_{1/2} = L/t_{1/2} E$, where $t_{1/2}$ is the time for photocurrent to decay to the half of its plateau value (see Fig. 3). The second method is the method of choice used in most experimental papers.

Results and Discussion

Figure 4 demonstrates the mobility concentration dependence for different thickness of a transport layer and clearly confirms the suggested explanation for the unusual mobility concentration dependence: the greater the thickness of the transport layer (and, hence, the lower contribution of dispersive transport), the lower is the value of n in Eq. 5. For thick layers this value becomes very close to 1 (see Fig. 5). In other words, transport in thin layers is not so sensitive to a small concentration of traps because the major fraction of carriers avoids traps. For this reason the mobility in thin layers does not drop significantly from the correspond-

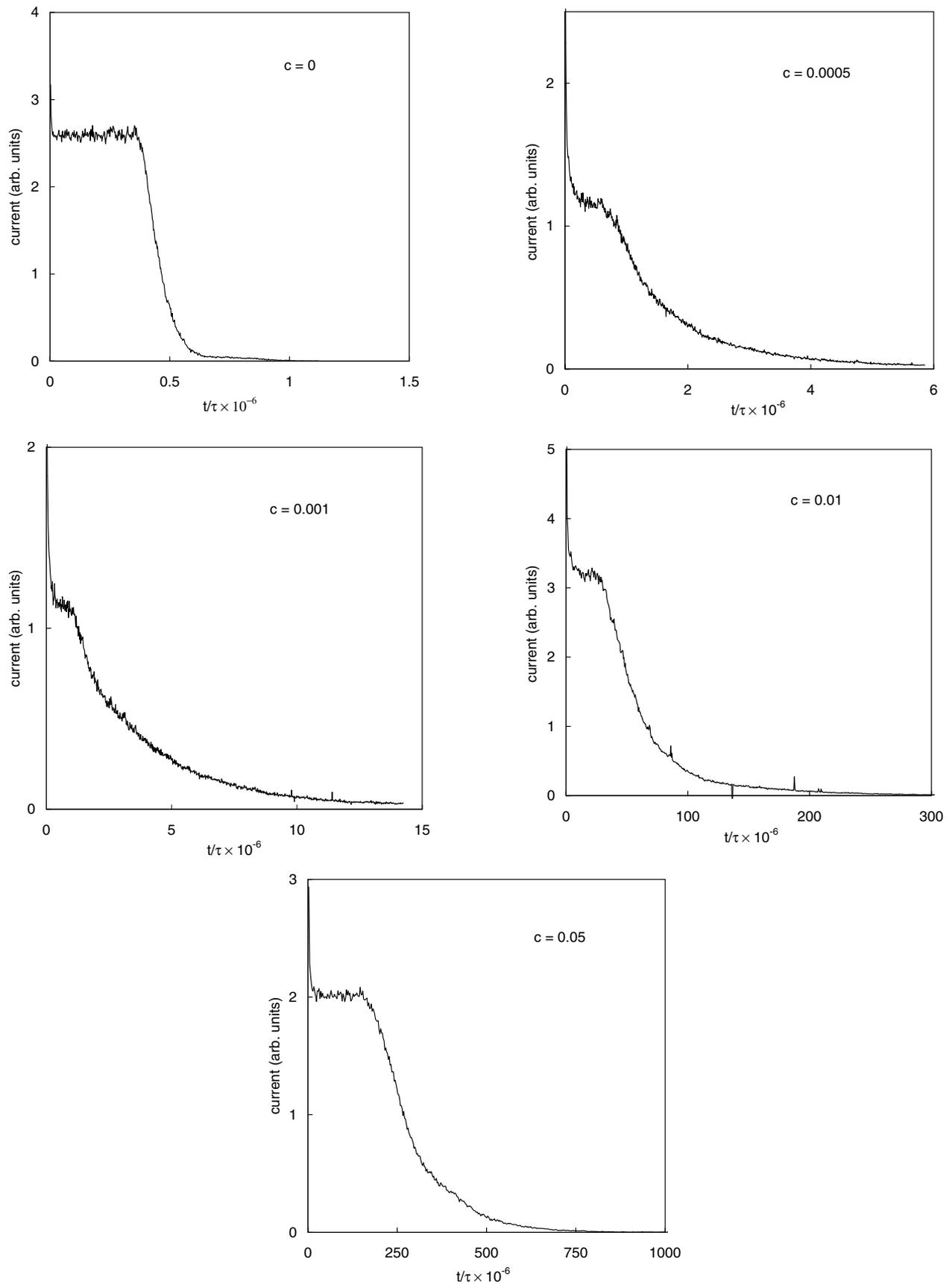


Figure 1. Photocurrent transients for transport layers with different fractions of sites, occupied by traps (indicated on plots); $\sigma/kT = 3.83$, $eaE/\sigma = 0.44$, $\Delta/kT = 10$ and transport layer thickness is 20,000 lattice planes (τ is the Miller-Abrahams time scale). If $T = 298$ K and $a = 10$ Å, then $\sigma = 0.098$ eV, $\Delta = 0.26$ eV, and $E = 4.3 \times 10^5$ V/cm.

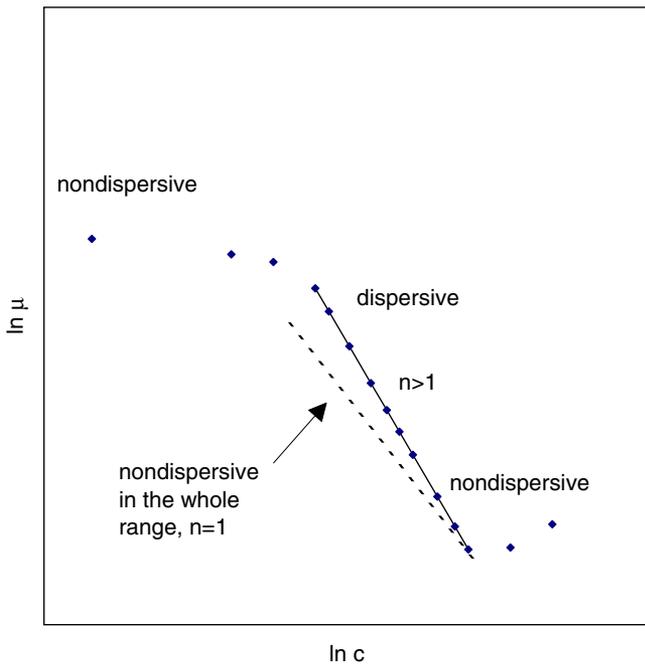


Figure 2. Typical experimental mobility dependence on the trap concentration (diamonds) and anticipated dependence for the nondispersive transport in the whole concentration range (broken line).

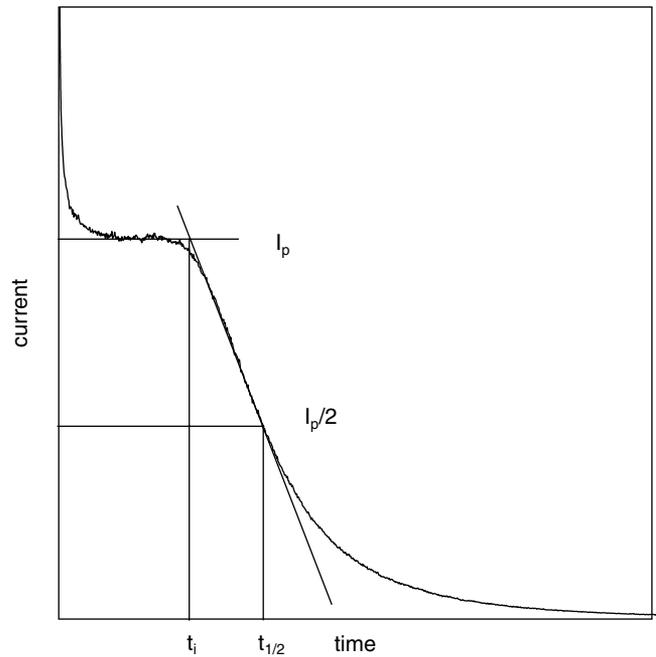


Figure 3. Two methods of mobility calculation from experimentally measured photocurrent transient: $\mu_i = L/t_i E$ and $\mu_{1/2} = L/t_{1/2} E$.

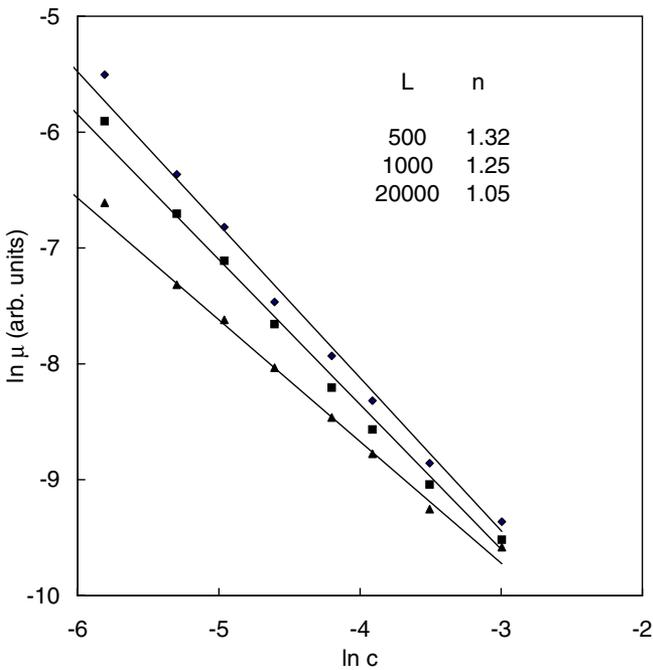


Figure 4. Dependence of μ_v on trap concentration for $\sigma/kT = 3.83$, $eaE/\sigma = 0.44$, $\Delta/kT = 10$, and different thickness L of a transport layer: 500 planes - diamonds, 1,000 planes - squares, and 20,000 planes - triangles.

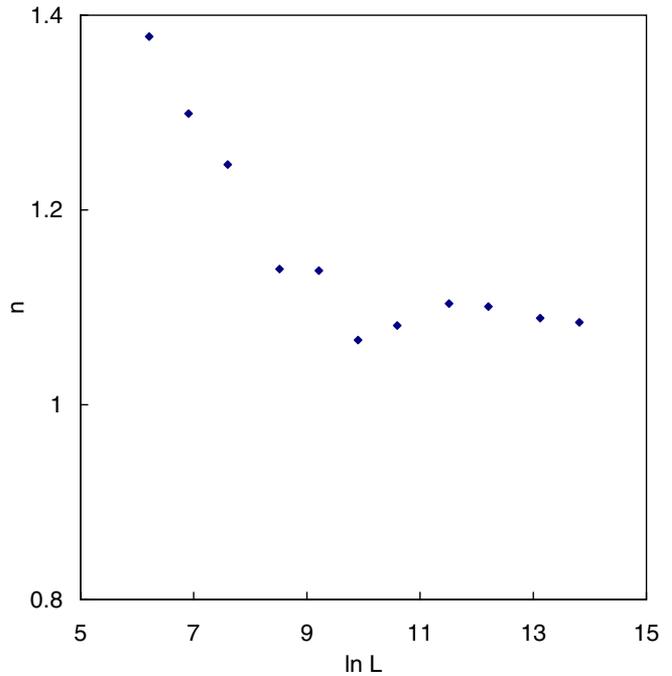


Figure 5. Dependence of n on the thickness L of the transport layer for $\sigma/kT = 3.83$, $eaE/\sigma = 0.44$, and $\Delta/kT = 10$.

ing value for the trap-free matrix. For high trap concentrations a major fraction of carriers undergo multiple trapping even in relatively thin layers. In this case, transport is essentially nondispersive, and the trap-induced decrease of the mobility does not differ significantly from the corresponding decrease in thick layers. Hence, the difference in mobility values for low versus

high trap concentrations is greater for thin layers (dispersive transport). This effect inevitably leads to a greater value of n for the dispersive transport in thin layers. Hence, the suggestion in Ref. 15, that the observed unusual concentration dependence “could only be explained by a new theoretical approach” seems to be a bit farfetched. The increase of n with increasing Δ ,

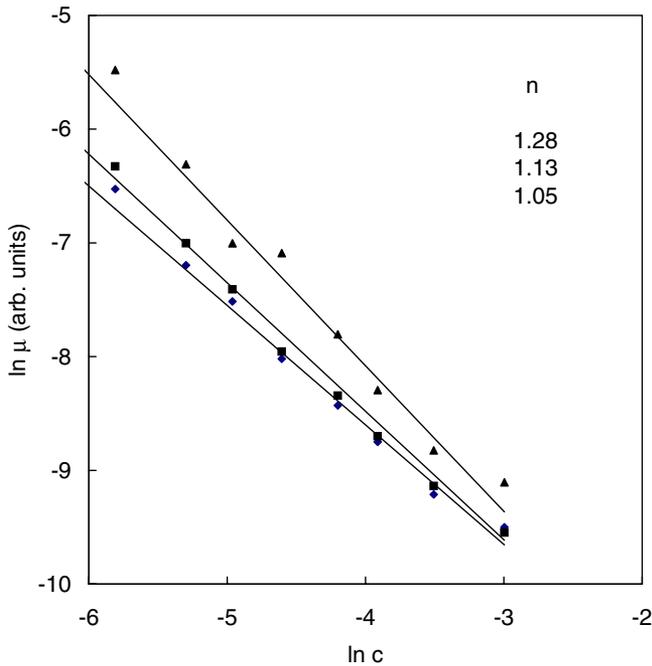


Figure 6. Mobility dependence on the trap concentration for $\sigma/kT = 3.83$, $eaE/\sigma = 0.44$, $\Delta/kT = 10$, and $L = 1,000,000$ lattice planes for different methods of mobility calculation: μ_v - diamonds ($n = 1.05$), $\mu_{1/2}$ - squares ($n = 1.13$), and μ_i - triangles ($n = 1.28$).

observed in Ref. 17, is quite understandable, because increased Δ leads to an increase in the dispersive component of charge transport.

Our simulation raises a very important question concerning the interpretation of experimental data. In previous discussions we have used the mobility μ_v , calculated from the average velocity of charge carriers. This mobility has a clear advantage over μ_i and $\mu_{1/2}$ because it derives from a theoretical definition. However, because it is impossible to determine μ_v directly from experimental data, for discussion of experimental results, values of μ_i (mainly) and $\mu_{1/2}$ (very rarely) are used. Our results show that the strong preference for the use of μ_i instead of $\mu_{1/2}$ leads, in some cases, to wrong conclusions. The danger in the use of μ_i is clearly demonstrated in Fig. 6, because even for the very thick transport layer (one million planes!) the value of n for μ_i differs significantly from 1. Figure 6 indicates that calculation of the mobility from $t_{1/2}$ seems to be a much more credible procedure; it should be used instead of extremely unreliable procedure that employs t_i . The overwhelming use of the intersection procedure undermines the credibility of the discussions of many experimental results.

Additional confirmation of our last statement could also be found in Ref. 15. We have already mentioned that for deep traps the mobility field dependence reported in this article has a linear form (Eq. 4) over the whole field range, in striking contrast to the theoretical prediction.¹³ This disagreement can be explained by the same phenomenon: a different contribution of dispersive transport for different field strengths (it is worth noting that for shallow traps with less dispersive transport the usual PF dependence was observed¹⁵). If this explanation is true, then we should expect: 1) transformation of the shape of the photocurrent transient with variation of the electric field, and 2) notable differences in the functional forms of the

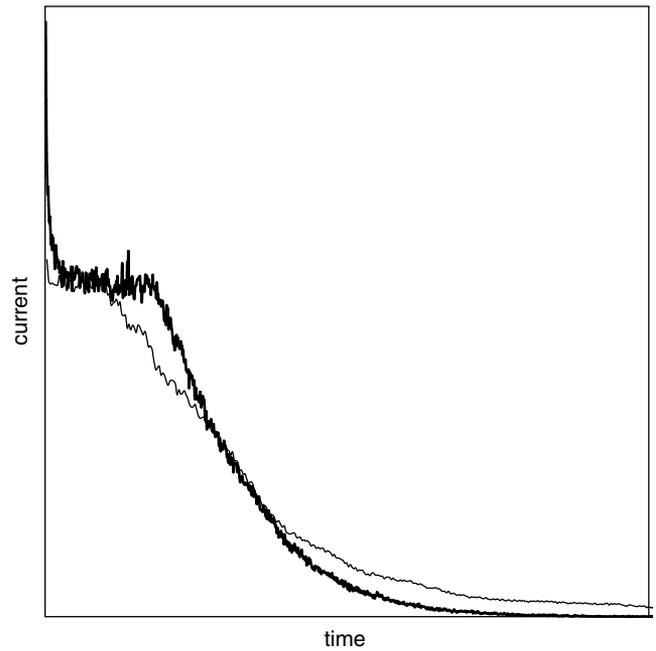


Figure 7. Photocurrent transients for $\sigma/kT = 3.83$, $\Delta/kT = 10$, $c = 0.01$, $L = 40,000$, and two values of eaE/σ : 0.021 (thin line) and 1.70 (thick line), correspondingly, with the time axis rescaled to make values of $t_{1/2}$ equal for both transients. Note the different shapes of transients.

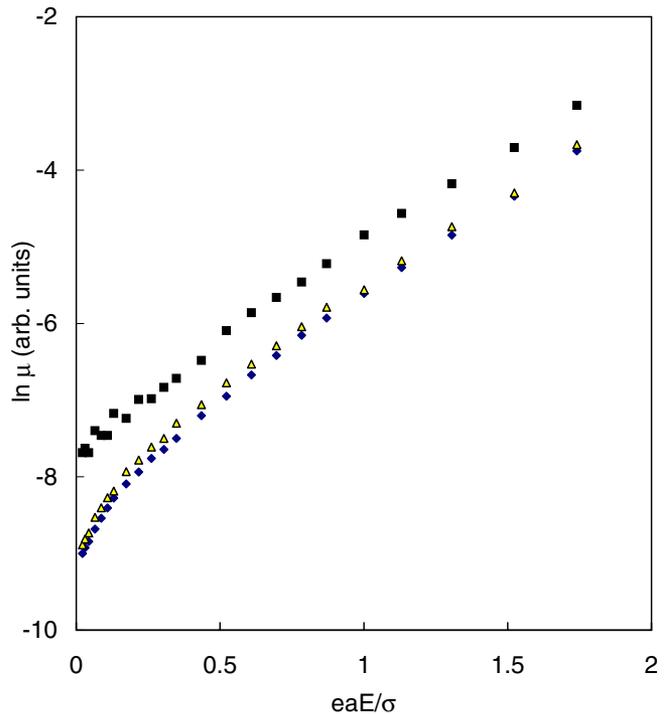


Figure 8. Mobility dependence on the electric field for $\sigma/kT = 3.83$, $\Delta/kT = 10$, $c = 0.01$, and $L = 40,000$ lattice planes, for different methods of mobility calculation: μ_v - diamonds, $\mu_{1/2}$ - triangles, and μ_i - squares.

$\mu_i(E)$ and $\mu_v(E)$ dependences. Figures 7 and 8 confirm these predictions. Again, the mobility, calculated from $t_{1/2}$ is much closer to the mobility calculated from the average MC velocity. The differences between μ_i and μ_v (and $\mu_{1/2}$) is most significant for small fields, so sig-

nificant that the functional dependence of μ_i (linear) is totally different from the functional dependence of μ_v and $\mu_{1/2}$ (usual PF dependence). Again, as in the case of the concentration dependence, use of μ_i distorts the true mobility field dependence.

The ultimate reason for this distortion is very simple: by definition, μ_i is sensitive to the particular shape of the transient, and overestimates the contribution of fast carriers. Hence, if in some parameter range (electric field, concentration of traps, or something else) the shape of transient changes significantly, then the use of μ_i for determining the functional dependence of the carrier mobility on this particular parameter is under great suspicion.

Conclusions

The dependence of carrier drift mobility in disordered dipolar materials on the concentration of traps has been studied using computer simulation. We found that the unusual concentration dependence, observed recently,^{15,17} is the result of a transition from dispersive to nondispersive charge transport with increasing trap concentration. Experimental tests of this result should be of the same nature as the computer simulation itself—measurements of carrier mobility for small trap concentrations in thick layers, much thicker than previously investigated; such measurements are possible²² for the transport systems studied in Ref. 17.

We have shown that in some situations mobility determined in the usual way or by the time at the intersection of 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 mobility, calculated by the time for the photocurrent to decay to half of its plateau value, more closely coincides with the usual definition of the mobility by the average carrier velocity, and thus should be used for discussion of experimental results. 

Acknowledgments. I first discussed ideas of this paper with Paul Borsenberger at our last meeting during the Albuquerque transport workshop in March 1998. As

usual, Paul was very enthusiastic and offered to provide the experimental test for the proposed explanation. He just did not have much time... With this article, I would like to pay tribute to the researcher whose efforts to large extent defined the whole area of the study of the charge carrier transport in disordered organic materials. This research, conducted in part at the Maui High Performance Computing Center, was partially sponsored by the US Air Force Research Laboratory, Air Force Material Command, under cooperative agreement F29601-93-2-0001, by the International Science and Technology Center grant 872-98, Russian Fund for Basic Research grant 99-03-32111, and the Albuquerque High Performance Computing and Educational Center. Discussions with V. M. Kenkre, D. H. Dunlap, and P. E. Parris are gratefully acknowledged.

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