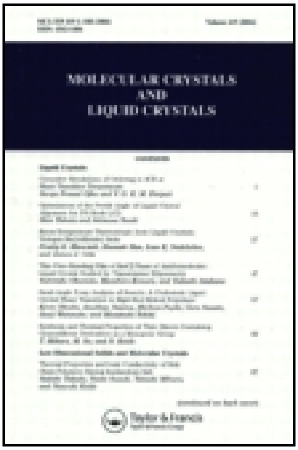

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Satoyuki Nomura [a] & Yasuhiko Shirota [a]

[a] Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka, 565, Japan

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Concentration Dependence of the Activation Energy for the Hole Drift Mobility of 9-Ethylcarbazole-3-carbaldehyde Hydrazones

SATOYUKI NOMURA and YASUHIKO SHIROTA*
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadaoka, Suita, Osaka 565, Japan

A new type of concentration dependence, *i.e.*, intersite-distance (ρ) dependence, of the activation energy for the hole drift mobility of the 9-ethylcarbazole-3-carbaldehyde diphenylhydrazone (ECH) and 9-ethylcarbazole-3-carbaldehyde methylphenylhydrazone (ECMH) dispersed in polycarbonate (PC) is reported. The activation energy for charge transport in the ECH or ECMH-doped PC systems gradually decreases with decreasing ρ for large values of ρ, becoming nearly constant for small values of ρ. This behavior contrasts with that for the 4-diphenylaminobenzaldehyde diphenylhydrazone (DPH)-doped PC system. Specific intermolecular interactions between ECH or ECMH molecules having a planar carbazole moiety at relatively high concentrations are suggested to be responsible for this concentration dependence of the activation energy.

Keywords: hole drift mobility, activation energy, concentration dependence, arylaldehyde hydrazone, carbazole moiety

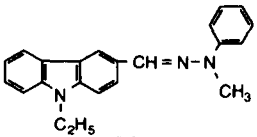
INTRODUCTION

Charge transport in organic disordered systems, both amorphous polymers and molecularly-doped polymer systems, where low molecular-weight organic materials are dispersed in polymer binders, has been a subject of recent extensive studies in view of both academic interest and practical application to electrophotography. It has generally been accepted that the charge-carrier drift mobility of organic disordered systems depends upon both electric field and temperature and that charge transport in organic disordered systems takes place by a thermally activated hopping process. In addition, the drift mobility of molecularly-doped polymer systems is affected by the intersite distance between charge-transport molecules dispersed in a polymer.

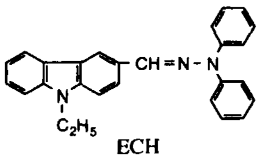
A few models have been proposed to explain the temperature and electric-field dependencies of the drift mobility in organic disordered systems, which include the Poole-Frenkel model,[1] the small-polaron model,[2,3] and the disorder formalism.[4,5]

Recently, the dependence of activation energy for charge transport on the concentration of transport molecules, *i.e.* intersite distance, has been studied. The activation energy for charge transport in some systems, *e.g.* 4-diethylaminobenzaldehyde diphenylhydrazone (DEH)-doped polycarbonate (PC) and 1-phenyl-3-*p*-diethylaminostyryl-5-*p*-diethylaminophenyl-2-pyrazoline (DEASP)-doped PC systems,[2,3,6,7] has been shown to be independent of the concentration of charge-transport molecules. In some systems, however, the activation energy is affected by the concentration of the transport molecule dispersed in a polymer binder, namely, the intersite distance between charge-transport molecules. The following intersite-distance (ρ) dependencies of the activation energy have been reported. (1) The activation energy decreases with increasing concentration, *i.e.* with decreasing ρ, of a charge-transport material in the N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD)-doped PC and 1,1-bis(di-4-tolylaminophenyl) cyclohexane (TAPC)-doped PC systems in the ranges from ρ=16 to 9 Å and from ρ=21 to 10 Å, respectively.[2,3,8-10] (2) The activation energy is constant for large values of ρ but decreases with decreasing ρ for small values of ρ.[11-13] The tri-*p*-tolylamine (TTA)-doped PC and 4-diphenylaminobenzaldehyde diphenylhydrazone (DPH)-doped PC systems have been reported to be the case, where the transition of the activation energy from a constant value to gradually decreasing values takes place at approximately ρ=15 Å for TTA and 12 Å for DPH systems. We have reported the following new type of intersite-distance (ρ) dependence of the activation energy for charge transport. That is, (3) the activation energy for charge transport in the 9-ethylcarbazole-3-carbaldehyde diphenylhydrazone (ECH)-doped PC system gradually decreases with decreasing ρ for large values of ρ, becoming nearly constant for small values of ρ.[13] These intersite-distance dependencies of the activation energy for charge transport described above have been explained in terms of the small-polaron model.[2,3,11-13]

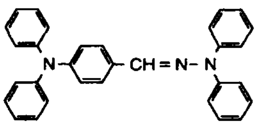
We report here that 9-ethylcarbazole-3-carbaldehyde methylphenylhydrazone (ECMH)-doped PC system also shows the same intersite-distance (ρ) dependence of the activation energy for the hole drift mobility as observed for the ECH-doped PC system. The present study provides another example of the new type of intersite-distance dependence of the activation energy for charge transport.



ECMH



ECH



DPH

EXPERIMENTAL

ECMH was prepared by the reaction of 9-ethylcarbazole-3-carbaldehyde with methylphenylhydrazine in ethanol at 80 °C for 2 hr and purified by recrystallization from benzene/ethanol.

The hole drift mobility was measured by the time-of-flight method for a layered device consisting of a charge-carrier generation layer (CGL) of x-type metal-free phthalocyanine dispersed in poly(ethylene-co-vinylchloride) and a charge-carrier transport layer (CTL) of the molecular glass or molecularly-doped PC.[13] The temperature was controlled with a temperature controller (Oxford ITC 502). The photocurrent was monitored with a digital storage scope, TDS 540A (Tektronix).

RESULTS AND DISCUSSION

Transient photocurrents (i_{ph}) as a function of time (t) observed for the ECMH-doped PC system were nearly nondispersive. The transit time (τ_t) was determined from the plot of log i_{ph} *vs.* log t based on the Scher-Montroll theory.[14] The hole drift mobility was calculated from the transit time, according to the expression $\mu=L^2/\tau_t V$, where L is the sample thickness and V the applied voltage. The intersite distance (ρ) was calculated on the basis of the assumption of a cubic form, according to the formula $\rho=(M/N_A Cd)^{1/3}$, where M is the molecular weight, N_A is the Avogadro constant, C is the fractional concentration of transport material and d is the density measured.

The experimental results were analyzed in terms of the small-polaron model. According to this model, the zero electric-field mobility is described as Eq. (1):

$$\mu(E{=}0) = (e\rho^2/kT)P(\omega/2\pi)\exp(-E_{act}/kT) = \mu_0\exp(-E_{act}/kT) \qquad (1)$$

where P is the charge-carrier jump probability when energy coincidence occurs between the two transport sites, ω is the phonon frequency, e is the electronic charge, k is the Boltzmann constant, T is the absolute temperature, and ρ is the intersite distance. The activation energy E_{act} is described as Eq. (2):

$$E_{act}=E_p/2-J \qquad (2)$$

where E_p is the polaron binding energy and J is the transfer integral, namely, the degree of electronic interaction between the adjacent transport molecules.

As observed for the ECH-doped PC system, the electric-field (E) dependence of the hole drift mobility of the ECMH-doped PC system was also found to follow $\exp(\beta E^{1/2})$, where β represents a proportional constant. The zero electric-field mobility $\mu(E=0)$ was obtained from the plots of log μ *vs.* $E^{1/2}$ by extrapolating to E=0.

The plots of log $\mu(E=0)$ *vs.* T^{-1} showed a good linear relationship. The E_{act} value for charge transport was then determined from the slope of the linear plots of log $\mu(E=0)$ *vs.* T^{-1} for each concentration of ECMH.

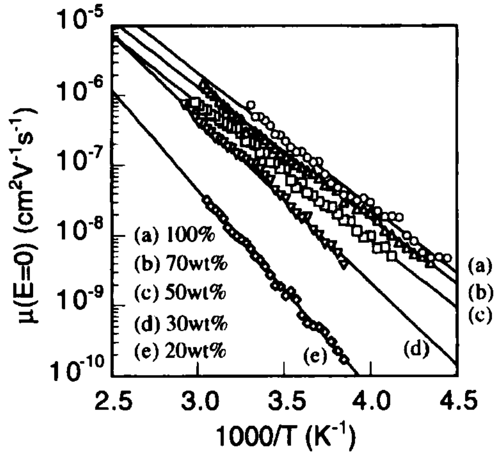


FIGURE 1 Plots of zero electric-field mobility $\mu(E=0)$ *vs.* T^{-1}.

Fig. 2 shows the intersite-distance (ρ) dependence of E_{act} for the ECMH-doped PC system. The intersite-distance dependencies of E_{act} for the ECH- and DPH-doped PC[13] systems are also included in Fig.2. The present result shows that the ECMH-doped PC system exhibits almost the same intersite-distance dependence of E_{act} as that for the ECH-doped PC system. The intersite-distance dependencies of E_{act} for both the ECH- and ECMH-doped PC systems contrast with that for the DPH system. That is, whereas E_{act} for the DPH system is almost constant for large values of ρ and then decreases with decreasing ρ for small values of ρ, E_{act} for both the ECH and ECMH systems decreases with decreasing ρ for relatively large values of ρ and then becomes nearly constant for small values of ρ. It should be noted that this behavior differs from that observed for *e.g.* the TPD-doped PC system, where E_{act} decreases monotonically with decreasing ρ.

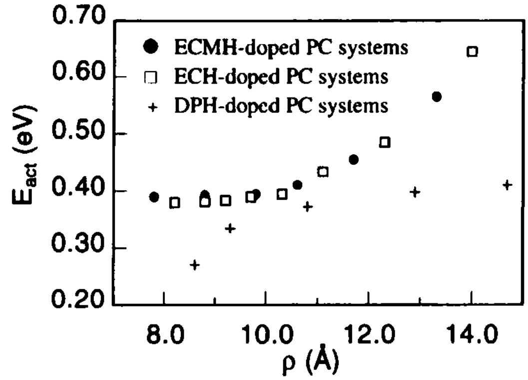


FIGURE 2 Intersite-distance dependencies of E_{act} for ECMH, ECH, and DPH-doped PC systems.

According to the small-polaron hopping model, the adiabatic and nonadiabatic regimes are defined as P in Eq. (1) being unity and smaller than unity, respectively. That is, in the adiabatic regime, the probability that a charge carrier hops is unity when energy coincidence takes place. On the other hand, in the nonadiabatic regime, the probability that a charge carrier hops is less than unity. The adiabatic and nonadiabatic regimes appear for large and small values of J in Eq. (2), respectively. Therefore, E_{act} for the adiabatic regime decreases with increasing J, but E_{act} for the nonadiabatic regime is almost independent of ρ, because J is too small to affect E_{act}. It has been understood that the DEH and DEASP systems exhibit the nonadiabatic charge-transport behavior but that the TPD and TAPC systems exhibit the adiabatic charge-transport behavior. The charge transport in the TTA and DPH systems has been understood as involving a transition at a certain intersite distance from the nonadiabatic regime at relatively large ρ values to the adiabatic regime at relatively small ρ values.

The result that E_{act} decreases with decreasing ρ in the region of large values of ρ shows that charge transport in both the ECH- and ECMH-doped PC systems basically exhibits the adiabatic behavior, suggesting that the J value for the ECH- and ECMH-doped PC systems is large enough to affect E_{act}. However, the experimental results show that E_{act} becomes nearly constant at small values of ρ. The transition from the nonadiabatic regime to the adiabatic regime with decreasing intersite distance is thought to be reasonable, but the opposite transition, *i.e.* the transition from the adiabatic to the nonadiabatic regime with decreasing ρ, seems to be unlikely, because J, which represents the degree of electronic interactions between the adjacent transport sites, is thought to increase with decreasing ρ. Both ECH and ECMH molecules contain a planar carbazole moiety in contrast to a nonplanar triphenylamine moiety in DPH. It is suggested that specific intermolecular π-electron interactions take place for the ECH and ECMH molecules at relatively high concentrations to form a hole-trap site that controls E_{act}, leading to a nearly constant value of E_{act} at small values of ρ.

SUMMARY

The present study shows that the ECMH-doped PC system exhibits the same intersite-distance dependence of E_{act} as observed for the ECH-doped PC system. That is, E_{act} for charge transport in the ECH and ECMH-doped PC systems gradually decreases with decreasing ρ for large values of ρ, becoming nearly constant for small values of ρ. It is suggested that specific intermolecular π-electron interactions of the ECH and ECMH molecules containing the planar carbazole moiety, which take place at relatively high concentrations, are responsible for this phenomenon.

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