Dyes and Pigments 9 (1988) 419–426

Charge-Transfer Complexes of *N*-Ethylcarbazole and Poly-*N*-vinylcarbazole with Dicyanonaphthoquinone Derivatives: Thermodynamic Parameters and Photofading Behaviour

Liyuan Han, Masaru Matsuoka* & Teijiro Kitao

Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai,
Osaka 591, Japan

(Received 7 October 1987; accepted 13 November 1987)

ABSTRACT

*Absorption spectra of the intermolecular charge transfer complexes of poly-*N*-vinylcarbazole and its monomeric analog,* N*-ethylcarbazole, with dicyanonaphthoquinone derivatives were measured in methylene chloride. The equilibrium association constants,* K_{CT} *and thermodynamic parameters accompanying the complex formation were evaluated. It was found that these CT complexes have broad absorption bands in the range 550–900 nm and exhibit extremely large* K_{CT} *values compared with other carbazole-2,4,7-trinitro-9-fluorenone complexes. The resultant CT complex showed good lightfastness when irradiated with visible light above 510 nm. There is a possibility that these complexes have applicability as coloring matters.*

1 INTRODUCTION

It is well known that poly-*N*-vinylcarbazole (PVCz) and its monomeric analog, *N*-ethylcarbazole (ECz), act as donors in charge-transfer (CT) complexes with various electron acceptors. In a previous publication[1] several naphthoquinone derivatives were newly prepared as acceptors and the intermolecular CT complexes of PVCz and ECz with the acceptors were examined. The relationships between the spectral changes and constitution

---

* To whom all correspondence should be addressed.

of the complexes were correlated with the results calculated by PPP MO technique.

In this investigation the equilibrium association constants and the thermodynamic parameters accompanying the CT complex formation in a solution have been determined to gain an insight into the nature of the complexes. In addition, the lightfastness of the resultant complexes was assessed in relation to their use as coloring matters.

2 RESULTS AND DISCUSSION

The absorption spectra of ECz and PVCz complexes with 5-nitro-2,3-dicyano-1,4-naphthoquinone (NDCNQ) or 2,3-dicyano-1,4-naphthoquinone (DCNQ) in methylene chloride are shown in Figs 1 and 2, respectively. For comparison the spectra of 2,4,7-trinitro-9-fluorenone (TNF) complexes of PVCz and ECz are also given in Figs 1 and 2. It is apparent in Figs 1 and 2 that the complexes of naphthoquinone derivatives have broad bands in the range 550–900 nm. It was described in our previous publication[1] that these visible to near-infrared bands are due to the formation of intermolecular charge-transfer complexes. Comparison of Fig. 1 with Fig. 2 indicates that the absorbance of the monomeric complex is higher than that of the polymeric complex. Also for any donor the absorption maximum of the NDCNQ complex shifts to a longer wavelength than that of the DCNQ complex. The CT complexes of PVCz–NDCNQ, PVCz–DCNQ, ECz–NDCNQ, and ECz–DCNQ investigated here were very stable in methylene chloride solution: the absorption maximum and the molar extinction coefficient of each complex remained unchanged even after 12 h.

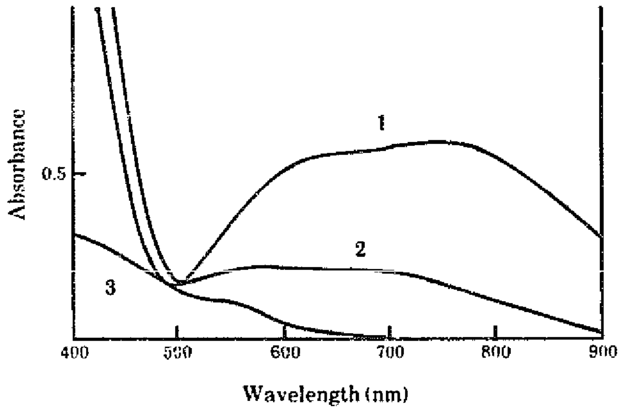

Fig. 1. Absorption spectra of intermolecular CT complexes in methylene chloride. Donor: ethylcarbazole; acceptor: 1, NDCNQ; 2, DCNQ; 3, TNF.

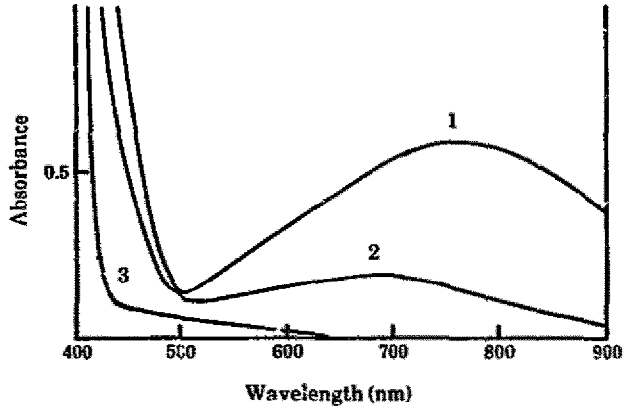

Fig. 2. Absorption spectra of intermolecular CT complexes in methylene chloride. Donor: poly-*N*-vinylcarbazole; acceptor: 1, NDCNQ; 2, DCNQ; 3, TNF.

In order to determine the molar ratio of the donor to the acceptor in the CT complex in the solution, the continuous variation method was applied to each system (Fig. 3). In the curve plotted for the absorbance at λ_{max} the maximum appears to be close to 50 mol % of the molar ratios of the acceptor to the sum of the acceptor and the donor, which indicates that one acceptor molecule is attached to one donor molecule. A 1:1 correspondence between the donor and acceptor molecules in the CT complex in the solution is thus established.

To facilitate quantitative comparison, the equilibrium association constant K_{CT} accompanying the CT complex formation has been

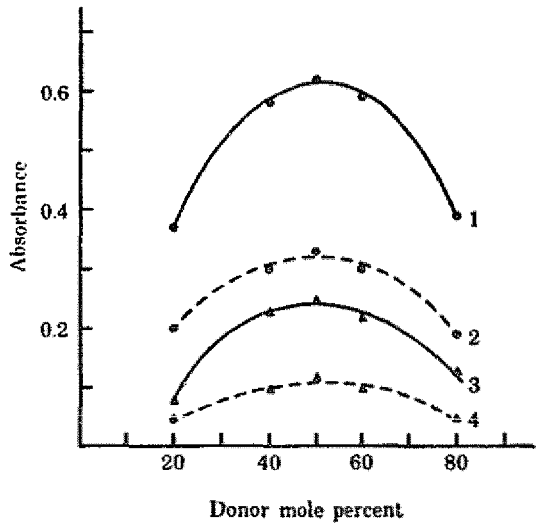

Fig. 3. Variation of absorbance with molar percentage of donor. Total molar concentration was maintained at 0·01M. 1, ECz-NDCNQ; 2, PVCz-NDCNQ; 3, ECz-DCNQ; 4, PVCz-DCNQ.

determined at various temperatures by the Benesi–Hildebrand method. The results are shown in Fig. 4. The data at each temperature measured fitted a linear relation in a graph. Furthermore, the extrapolation of these lines apparently converged to meet at a point on the ordinate, indicating that ε is independent of the temperature in the range investigated. The values of K_{CT} are dependent on temperature and increase with decreasing temperature: the CT complex formation is exothermic. The value of K_{CT} can be obtained by eqn (1) proposed by Benesi & Hildebrand,[2]

$$[A]_0 \frac{l}{A_\lambda} = \left(\frac{1}{\varepsilon} K_{CT}[D]_0\right) + \frac{1}{\varepsilon} \qquad (1)$$

in which $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor and the donor; l, A_λ and ε represent the path length, the absorbance of the CT complex at λ and the molar extinction coefficient of the complex at λ, respectively. Equation (1) is applicable only when a 1:1 complex is formed

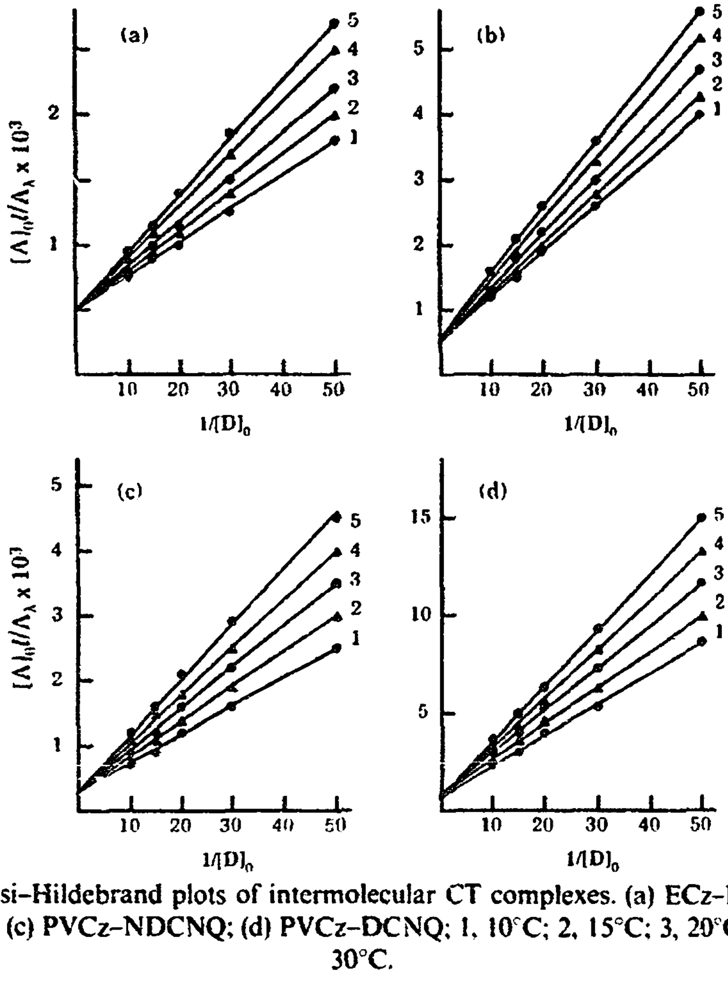

Fig. 4. Benesi–Hildebrand plots of intermolecular CT complexes. (a) ECz-NDCNQ; (b) ECz-DCNQ; (c) PVCz-NDCNQ; (d) PVCz-DCNQ; 1, 10°C; 2, 15°C; 3, 20°C; 4, 25°C; 5, 30°C.

and $[D]_0 \gg [A]_0$ is established. van't Hoff plots of K_{CT}, $\ln K_{CT}$ vs $1/T$ plots, in the course of the CT complex formation are shown in Fig. 5. The thermodynamic parameters, ΔH and ΔS, which accompany the formation of a CT complex, can be evaluated from the K_{CT} value and its temperature dependence using eqn (2).

$$\ln K_{CT} = (-\Delta H/RT) + (\Delta S/R) \tag{2}$$

The values of K_{CT}, ΔH and ΔS obtained for the various donor–acceptor complexes are summarized in Table 1 together with the data for TNF complexes reported previously by Okamoto *et al.*[3] With TNF complexes, good agreement between our results and those of Okamoto *et al.* can be seen. The equilibrium constants of the acceptors for a common donor increase in the following order: TNF < DCNQ < NDCNQ. A very much greater extent of association by NDCNQ can be observed compared with the other acceptors, DCNQ and TNF. It is obvious that a substantial increase in the association constant can be created in NDCNQ upon introduction of a nitro group, which withdraws electrons from the naphthoquinone ring, and hence gives the ring a stronger electron-accepting character. The values of K_{CT} obtained for the complexes of ECz with tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ), which are the acceptors commonly used, were reported to be 2·8 and 3·5, respectively.[3] Thus the values found in ECz–NDCNQ and ECz–DCNQ complexes, in particular the former complex, are considerably higher than these values. When the equilibrium constant of the polymeric complex is compared with that of the corresponding complex of unit segment, ECz, the former is always smaller

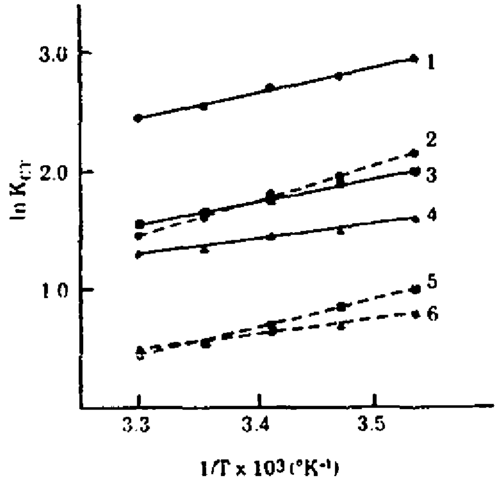

Fig. 5. Relationship between ln K_{CT} and reciprocal of absolute temperature for formation of the CT complexes. 1, ECz–NDCNQ; 2, PVCz–NDCNQ; 3, ECz–DCNQ; 4, ECz–TNF; 5, PVCz–DCNQ; 6, PVCz–TNF.

TABLE 1
Thermodynamic Constants for the Formation of CT Complexes

Donor	$[D]_0$(M)	*Acceptor*	$[A]_0$ (10^3M)	ε_{max} (*cm*/M)	K_{CT}(M^{-1}) *at 15°C*	$-\Delta H$ (*kcal/mol*)	$-\Delta S$ (*e.u.*)
ECz	0·02–0·1	NDCNQ	1·0	2000	16·8	4·4	9·8
PVCz	0·02–0·1	NDCNQ	1·0	2900	7·1	5·9	16·4
ECz	0·02–0·1	DCNQ	2·0	1600	6·6	3·5	8·6
PVCz	0·02–0·1	DCNQ	2·0	2200	2·4	5·0	15·7
ECz	0·02–0·1	TNF	2·0	1900	4·6	2·7	6·4
ECz[a]	0·02–0·1	TNF	2·0	2000	4·3	2·6	6·2
PVCz	0·04–0·2	TNF	2·0	1300	2·0	2·4	6·8
PVCz[a]	0·05–0·2	TNF	3·0	1200	2·1	2·3	6·8

[a] Taken from Ref. 3.

than the latter for any acceptor. Such a trend was observed in other systems and interpreted in terms of steric hindrance of the polymer backbone in the complex formation.[3–5]

For all the CT complexes investigated the complex formation is accompanied by negative enthalpy and entropy terms. Accordingly, the association process is favorable in the energetic situation and is unfavorable with respect to the entropy term. For any donor, the ΔH value of the NDCNQ complex is more negative by $-0{\cdot}9\,\mathrm{kcal\,mol^{-1}}$ than that of the DCNQ complex. This difference in ΔH between NDCNQ and DCNQ is ascribed to the electron-withdrawing character of the nitro group present in the naphthoquinone ring. Although the values of $-\Delta H$ of the complexes with PVCz are larger than those of ECz, due probably to a small enhancement in the electron-donating character of PVCz compared with that of ECz,[3] the values of K_{CT} of the polymeric complex are considerably smaller than those of the corresponding monomeric complex. This situation arises from the extremely large $-\Delta S$ value for the polymeric complexes. The large decrease in ΔS value is due presumably to the conformational change of the polymer chains, that is chain folding, when the polymeric donor interacts with the naphthoquinone acceptor.

Lightfastness of the CT complexes, as well as absorption wavelength and absorbance, is an important factor when the complexes are applied as coloring matters. The lightfastness values of the PVCz–NDCNQ complexes are represented in Fig. 6 together with those of the PVCz–TNF complex. The absorbance of the PVCz–TNF complex was almost unchanged with exposure time. With the complex of PVCz and NDCNQ, the absorbance decreased to *c.* 85% of its original value when the sample was irradiated without filter for 20 h and its greenish color changed to a yellowish hue. It is

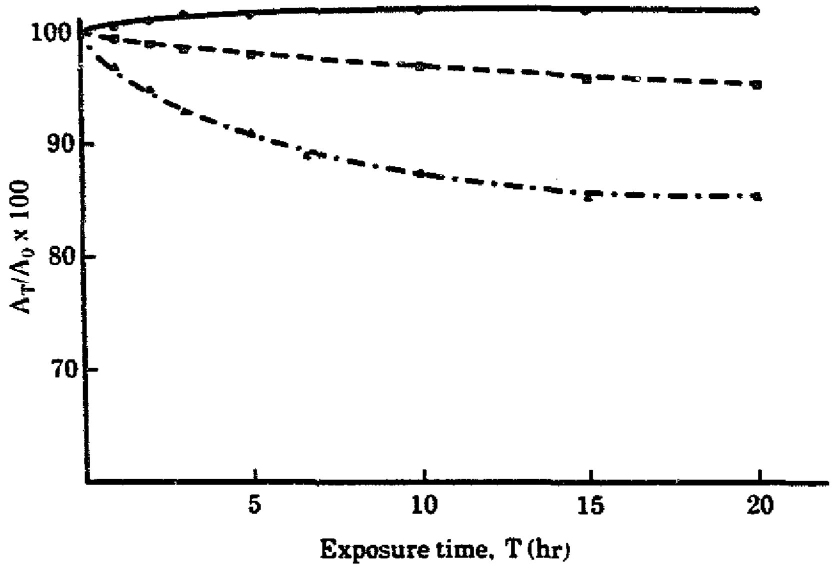

Fig. 6. Photofading of CT complexes of PVCz on irradiation with a xenon lamp. ——, TNF without filter; - - - -, NDCNQ with filter; — · — · —, NDCNQ without filter. A_0 and A_T represent the values at times 0 and T, respectively.

known that naphthoquinone decomposes via a semiquinone radical on irradiation with light, in particular UV light.[6] Consequently, when the filter, which can cut off light below 510 nm, was attached and only CT absorption bands were excited, the CT complex was found to be very stable on irradiation. Thus there is a possibility that the CT complex dyes examined here are practically applicable as coloring matters.

3 EXPERIMENTAL

3.1 Materials

N-Ethylcarbazole (ECz; Tokyo Kasei Co.) was recrystallized three times from methanol in the presence of active carbon and vacuum-dried at 40°C, m.p. 68°C (literature m.p. 68°C).

Poly-*N*-vinylcarbazole (PVCz) was prepared by the polymerization of a 0·5M solution of *N*-vinylcarbazole (Tokyo Kasei Co.) in benzene with 1 mol% of azobisisobutyronitrile as initiator under a nitrogen atmosphere at 60°C for 5 h, and the resultant polymer was reprecipitated three times from benzene solution with methanol. The degree of polymerization determined by viscosity measurements was about 1600.

5-Nitro-2,3-dicyano-1,4-naphthoquinone (NDCNQ), 2,3-dicyano-1,4-naphthoquinone (DCNQ), and 2,4,7-trinitro-9-fluorenone (TNF) were used as acceptor compounds. NDCNQ and DCNQ have been reported in our previous study. Guaranteed reagent grade TNF (Tokyo Kasei Co.) was used without further purification.

Methylene chloride (guaranteed reagent grade, Tokyo Kasei Co.) was used as a solvent for the absorption measurements.

3.2 Method

The absorption spectra and optical density were measured in a Shimadzu spectrophotometer model UV-240 using a 1-cm glass cell. The cell compartments were maintained at 10, 15, 20, 25 and 30°C by a circulating water bath.

3.3 Measurements of photofading

The CT complexes of PVCz–NDCNQ and PVCz–TNF were coated on a glass plate, the absorbance of the coated plate being controlled to optical density of 1.

A xenon lamp (500W, USHIO XB-50101AA) was used as a light source. The distance from the plate to the lamp was kept constant at 60 cm. The sample was irradiated with and without the filter (Toshiba Y-51) which can cut off light below 510 nm.

REFERENCES

1. Matsuoka, M., Yodoshi, T., Han, L. & Kitao, T., *Dyes and Pigments*, **9** (1988), 343.
2. Benesi, H. A. & Hildebrand, J. H., *J. Amer. Chem. Soc.*, **17** (1949), 2703.
3. Okamoto, K., Ozeki, M., Itaya, A., Kusabayashi, S. & Mikawa, H., *Bull. Chem. Soc. Japan*, **48** (1975), 1362.
4. Enomoto, T. & Hatano, M., *Makromol. Chem.*, **175** (1974), 57.
5. Rembaum, A., Hermann, A. M. & Haack, R., *J. Polym. Sci. Part A-1*, **6** (1968), 1955.
6. Tickle, K. & Wilkinson, F., *Trans. Faraday Soc.*, **61** (1965), 1981.