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Charge transfer complex formation between *p*-chloranil and 1,*n*-di(9-anthryl)alkanes

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Abstract

Dimer model compounds of polyvinylanthracenes (1,n-di(9-anthryl)) alkanes, when n = 1-5) were synthesized to model the effects of distance and orientation between anthracene groups in polymeric systems. Charge transfer (CT) complexes of anthracene, 9-methylanthracene and 1,*n*di(9-anthryl)alkanes with *p*-chloranil (*p*-CHL) have been investigated spectrophotometrically in dichloromethane. The colored products are measured spectrophotometrically at different wavelength depending on the electronic transition between donors and acceptor. The formation constants of the CT complexes were determined by the Benesi–Hildebrand equation. The thermodynamic parameters were calculated by Van't Hoff equation. Stochiometries of the complexes formed between donors and acceptor were defined by the Job's method of the continuous variation and found in 1:1 complexation with donor and acceptor at the maximum absorption bands. © 2005 Elsevier B.V. All rights reserved.

Keywords: Charge transfer complexes; 1,n-Di(9-anthryl)alkanes; p-Chloranil; Spectrophotometrically determination

1. Introduction

Photoconductive polymers are used commercially in electrophotography and as storage media for light-weight batteries and photovoltaic cells for solar energy conversion [1,2]. Photoconductive polymers absorb radiation in the UV region. In order to generate hole carriers and bring absorption into the visible region, dopants are added. Photoconductive polymers can be doped with electron acceptors to form electron donor–acceptor (EDA) complexes [3]. Charge transport in doped polymer systems is visualized as a donor–acceptor process. Charge transfer (CT) processes to generate positively charged dopant molecules, which are radical cations in the polymer [4]. Optical absorption of radiation in the CT (visible region) by the EDA complexes gives photocarrier generation [5].

The formation of EDA complexes is readily apparent from the observation of new optical absorptions when electron

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donors (D) are mixed with electron acceptors (A) [6,7]. Colors accompany complex formation in solution, as a result of electronic interchanges between components [8].

EDA type complexes have important conductive properties in many types of chemical reactions. EDA complexes are commonly found as intermediates in a variety of reactions involving electron rich species or donors, such as nucleophiles and bases, and electron deficient acceptors [6,8]. Aromatic donors readily form EDA complexes with various types of π acceptors, such as chloranil and tetracyanoethylene (TCNE) [9]. EDA complexes promote reactivity by bringing the reactants together and encouraging the correct orbital overlap required for electronic reorganization [10].

EDA complexes have great attention for non-linear optical materials and electrical conductivities [11–15]. And also EDA interactions play an important role in the field of drugreceptor binding mechanism [16].

In this work, dimer model compounds of polyvinylanthracenes (1,n-di(9-anthryl)alkanes, when n = 1-5) were synthesized to model the effects of distance and orientation between anthracene groups in polymeric systems. Formation constants, stochiometries, thermodynamic parameters of the

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complexes between dimer compounds and *p*-chloranil were determined.

2. Experimental

2.1. Apparatus

A Hewlett-Packard HP8452A diode array spectrophotometer was used for UV–vis spectra using dichloromethane as the solvent. Proton (¹H) and ¹³C NMR spectra were obtained with a Bruker AC300F spectrometer using CDCl₃ solvent (Cambridge Isotopes).

2.2. Materials

Anthracene (M1) (Merck), 9-methylanthracene (M2) (Merck), p-chloranil (Merck), were used as bought. Dichloromethane used as solvent was spectroscopic grade. 1,n-Di(9-anthryl)alkanes were synthesized as below.

2.2.1. Di(9-anthryl)methane (1)

9-Anthrylmagnesium bromide was prepared by reacting 0.0166 moles of magnesium with 0.0062 moles of 9bromoanthracene in 30 ml of anhydrous ethyl ether for 24 h at room temperature with a small amount of iodine to initiate the reaction. Then, 0.0062 moles of 9-(chloromethyl)anthracene in 40 ml of anhydrous benzene were added to the cream colored grignard reagent and refluxed for 15 h. The reaction mixture was then cooled and extracted with 0.1 M HCl (50 ml). The yellow precipitate was filtered through a Buchner funnel and the final di(9-anthryl)methane product was isolated by recrystallization from toluene and then chloroform.

2.2.2. 1,2-Di(9-anthryl)ethane (2)

1,2-Di(9-anthryl)ethane was synthesized by reductive dimerization of 9-anthraldehyde with LAH refluxing 3 h in THF. The product was purified by recrystallization from toluene and chloroform.

2.2.3. 1,3-Di(9-anthryl)propane (3)

Trans-1,3-di(9-anthryl)propenone was prepared according to the literature procedure [17]. The compound was reduced by sodium borohydride in tetrahydrofuran to 1,3di(9-anthryl)propan-1-ol and 1,3-di(9-anthryl)propan-1-one. In the last step, these two compounds were reduced to the 1,3-di(9-anthryl)propane with LAH/AlCl₃ in ethyl ether.

2.2.4. 1,4-Di(9-anthryl)butane (4) and 1,5-di(9-anthryl)pentane (5)

1,4-Di(9-anthryl)butane and 1,5-di(9-anthryl)pentane were prepared via the formation of di-grignard reagents from 1,*n*-dibromoalkanes (n = 4 and 5) followed by reaction with anthrone. The compounds were purified by column

chromatography on alumina with hexane/dichloromethane eluting fractionally.

2.3. Stoichiometric relationship

The stoichiometries of the 1,*n*-di(9-anthryl)alkanes with chloranil were investigated. The method of continuous variations as given by Job's plot [18] is used to establish the stoichiometries of the complexes. Equimolar samples of anthracene, 9-methylanthracene, di(9-anthryl)alkanes and chloranil were prepared separately in methylene chloride. The concentrations of the sample were dependent on the solubility of the individual compounds in CH₂Cl₂. Aliquots of solutions were varied alternately from 0.2 to 0.8 ml for donor and chloranil solutions to hold the total volume at 1 ml in the cuvette by using a 1 ml syringe. Average optical densities were calculated from three runs on the same sample and average values at 812-820 nm were subtracted from the average values at the maxima.

2.4. Equilibrium constants

The Benesi–Hildebrand equation [19] was used to calculate equilibrium constants for the formation of EDA complexes of the anthracene, 9-methylanthracene and the series of 1,*n*-di(9-anthryl)alkanes. In these experiments, the electron acceptor (chloranil) was used at high concentration (initially, \sim 0.02 M) and the donor anthracenes were kept at a constant concentration which was always at least 20 times smaller than the concentration of chloranil. Chloranil background was measured before each spectrum was taken.

In the method for calculation of the equilibrium constants of EDA complexes using the Benesi–Hildebrand equation, 10 ml stock solutions of dianthryl in dichloromethane were prepared and 1 ml of the solution was placed in a 1 cm UV–vis cuvette. Chloranil was added to the 1 ml cuvette sample at ~21 mM concentration. The concentration of chloranil was decreased during the experiment by adding 0.1 ml divisions of the stock donor solution to the cuvette, which was used for measurement. The UV–vis spectrum was measured after each addition of 0.1 ml of solution. About 15 dilutions were run with each anthracene. The reverse concentration method, which involves keeping the chloranil concentration constant and adding a solution of anthracene compound to the sample cuvette, was not possible due to the low solubilities of the dianthrylalkanes (when n = 1 and 2).

2.5. Thermodynamic constants

Van't Hoff and Beer–Lambert equations were used to calculate thermodynamic parameters for the EDA complexes of anthracene compounds with chloranil.

Measurements were run at 0, 7, 14, 21, 28 and 35 $^{\circ}$ C (except for di(9-anthryl)methane due to precipitation at 14 $^{\circ}$ C). Samples of the anthracene series of compounds with chloranil were prepared in volumetric flasks and placed into

a 1 cm UV–vis cuvette. Measurements at 0 °C were run in a glove bag under nitrogen atmosphere in order to prevent condensation on the cuvette. Chloranil was used as a background. Samples were measured three times at the same temperature. From the averaged data was subtracted the absorbance due to anthracene compounds in the solvent (CH₂Cl₂) measured separately. The concentrations were corrected for the volume changes at the different temperature. The constants were calculated by plotting ln(ABS/ \in) – 2 ln(A_0 – ABS/ \in)(D_0 – ABS/ \in) versus 1/*T* (K).

3. Results and discussions

The absorption spectra of solutions containing anthracene series compounds and *p*-chloranil together exhibit new absorptions at longer wavelength than either the donors ($\lambda < 400 \text{ nm}$) or the acceptor ($\lambda < 450 \text{ nm}$) alone. EDA complexes between chloranil and anthracene has highest transition energy (lower $\lambda = 632 \text{ nm}$) of the other anthracene compounds, di(9-anthryl)methane is second ($\lambda = 670 \text{ nm}$) and 1,2-di(9-anthryl) ethane is third ($\lambda = 674 \text{ nm}$). Transition energies of other dianthracene compounds are lowest ($\lambda = 680 \text{ nm}$).

The new and broad absorptions indicates that the formation of electron donor–acceptor (EDA) complexes. Anthracene series compounds are relatively electron rich and *p*-chloranil are relatively electron poor compounds. When a solution containing both an electron rich and electron poor compound, they tend to associate with one another interaction known as EDA complexes. The interactions of all studied donor compounds with *p*-chloranil in dichloromethane gave different color from the original mention charge transfer complex formation.

The new and low energy absorptions observed in solutions containing both donor and an acceptor have been described by Mulliken [20] as charge transfer transitions involving the



Scheme 1. Charge transfer transitions for HOMOs of the donor compounds and LUMOs of the acceptor compounds.

excitation of an electron on the donor to an empty orbital on the acceptor. This is shown schematically in Scheme 1 in which hv_{CT} depicts the energy of the CT transitions. The lowest energy CT transition will involve promotion of an electron residing in the highest occupied molecular orbital (HOMO) of the donor to the acceptor as shown for hv_{CT} . Charge transfer transitions involving electrons in lower energy orbitals also are possible and would result in higher energy CT transitions as shown hv_{CT}^1 .

The interaction between the donor and acceptor gave $\pi - \pi^*$ transitions by the formation of radical ion pairs as shown in Scheme 2.

The stoichiometries of the EDA complexes of the series of anthracene compounds with chloranil was determined by the methods of continuous variations and shown to be 1:1 and shown in Fig. 1. EDA complexes of dimer compounds with chloranil showed formation constants approximately double these of anthracene and 9-methylanthracene, which correlates with the number of anthracene groups present.

The Benesi–Hildebrand equation was used for the determination of formation constants (K) and extinction coefficient, (ε), for the complexetion between anthracene and chloranil. The association constants were evaluated at wavelength formed complex for each donor and acceptor using the



Scheme 2. The molecular structure of compound and charge transfer transition between donor and acceptor.



Fig. 1. The plot of Job's method for methylanthracene (MEA) and 1,4-di(9anthryl)butane (DAB) with *p*-CHL.

equation given below.

$$\frac{[D_{\rm o}]}{\rm ABS} = \frac{1}{K\varepsilon[A_{\rm o}]} + \frac{1}{\varepsilon} \text{ or } \frac{[A_{\rm o}]}{\rm ABS} = \frac{1}{K\varepsilon[D_{\rm o}]} + \frac{1}{\varepsilon}$$

where $[A_o]$ is the concentration of the acceptor; $[D_o]$ the concentration of the donor; ABS the absorbance of the complex; \in_{CT} the molar absorptivity of the complex formed and K_{CT} is the association constant of the complex. On plotting of the values $[D_o]/ABS$ versus $1/[A_o]$, straight lines were obtained in Fig. 2 from which molar absorptivity, correlation coefficient and association constant given in Table 1. The slopes and $K\varepsilon$ values were calculated from the Benesi–Hildebrand plots which used a high concentration of acceptor and low concentration of donor.

The slopes of the Benesi–Hildebrand plots for the dianthryl compounds were around 0.24×10^{-3} to give a $K\varepsilon$ value of $4170 \,\mathrm{M^{-1} \, cm^{-1}}$ l. The slopes of the Benesi–Hildebrand plots for the monoanthracene compounds were around 0.472×10^{-3} to have a $K\varepsilon$ value $2120 \,\mathrm{M^{-1} \, cm^{-1}}$ l. The calculated $K\varepsilon$ for chloranil complexes of dianthryl compounds were, thus, about double the values for monoanthracene compounds. The values for anthracene and 9-methylanthracene were expected to be half of the dianthryl compounds, which have twice number of anthracene groups in each molecule.

 $K_{\rm BH}$ values of the complexes of anthracene and 9methylanthracene with chloranil are about 1.70 and $K_{\rm BH}$



Fig. 2. Benesi–Hildebrand plot of [donor]/absorbance vs. 1/[chloranil] at the maximum wavelength (nm) for EDA complex of anthracene series compounds and chloranil (ANH: **M1**, MEA: **M2**, DAM: **1**, DAE: **2**, DAR: **3**, DAP: **5**).

values of di(9-anthryl)alkanes are around 3.3 which is about double of the mono anthracene compounds. Anthracene compounds with chloranil forms more EDA complexes than EDA complexes of anthracene compounds with TNM according to the $K_{\rm BH}$ values of the complexes because anthracene compounds form stronger complexes with chloranil than TNM [21].

The small values of the intercept which are close to zero in these graphs causes large uncertainty in the values of the extinction coefficients so that ε of the EDA complexes could not be determined exactly. Therefore, the average value of the intercepts found for all graphs was used to approximate ε , which was assumed to be independent of the anthracene used.

The ΔS values in di(9-anthryl)alkanes show that the two anthracene groups behave independently and do not interfere one another in complexation for n > 2. The space between two anthracene ring allows complex formation of one anthracene group which is not affected by the presence of the other anthracene ring, except for di(9-anthryl)methane.

The thermodynamic constants of the electron donoracceptor complexes of anthracene compounds with chloranil were determined by Van't Hoff equation. Enthalpies (ΔH) and entropies (ΔS) of complex formation were determined using the Van't Hoff and Beer–Lambert equations for the

Table 1

Least-squares calculated slopes and $K\epsilon$ and λ_{max} values of anthracene–chloranil complexes at λ_{max} for Benesi–Hildebrand plots (ϵ assumed to be 1240 M⁻¹ cm⁻¹)

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Compounds-chloranil	Slope $\times 10^{-3} (1/K\varepsilon)$	Kε	r^2	$K_{ m BH}$	λ _{max} (nm)	
Anthracene	0.475 ± 0.013	2100 ± 60	0.993	1.70 (5) ^a	632	
Methylanthracene	0.468 ± 0.0091	2140 ± 40	0.996	1.72 (4)	680	
DAMethane	0.2565 ± 0.0091	3900 ± 130	0.990	3.14 (11)	670	
1,2-DAEthane	0.227 ± 0.0104	4400 ± 190	0.979	3.55 (16)	674	
1,3-DAPropane	0.2349 ± 0.0073	4260 ± 130	0.990	3.43 (10)	678	
1,4-DAButane	0.2492 ± 0.0078	4010 ± 120	0.990	3.24 (10)	678	
1,5-DAPentane	0.253 ± 0.016	3950 ± 230	0.960	3.19 (19)	680	

^a Determined to be 1.0 at 25 °C, with [anthracene]/[chloranil] \geq 30 [23].

Table 2
Van't Hoff experiments-calculated slopes and intercepts of the anthracene series compounds-chloranil complexes

-	-	-	-	-		
Compound-chloranil	Slope	Intercept	r^2	$\Delta H (\mathrm{kcal}\mathrm{mol}^{-1})$	ΔS (eu)	$K_{(calc.)}$ 21 °C
Anthracene	1206.7 ± 26	$-4.216 \pm .010$	0.998	$-2.40(6)^{a}$	$-8.4(1)^{a}$	$0.89 \pm .24$
Methylanthracene	1352.8 ± 97	$-4.31 \pm .040$	0.960	-2.69(19)	-8.6(1)	$1.34 \pm .62$
DAMethane	1422.3 ± 39	$-4.379 \pm .014$	0.997	-2.83 (8)	-8.7(1)	$1.58\pm.32$
1,3-DAPropane	1288 ± 16.7	$-3.662 \pm .006$	0.999	-2.56 (3)	-7.3 (1)	$2.05 \pm .23$
1,4-DAButane	1298.8 ± 33	$-3.741 \pm .012$	0.997	-2.58 (7)	-7.4 (1)	$1.97 \pm .34$
1,5-DAPentane	1325.6 ± 38	$-3.752 \pm .017$	0.993	-2.63 (8)	-7.5 (1)	$2.13\pm.42$

^a $\Delta H = -2.7 \pm 0.3$ kcal/mol and $\Delta S = -8.7 \pm 0.8$ eu [23].

series of anthracenes with chloranil.

$$\frac{\ln(ABS)}{\varepsilon} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} + \ln\left(D_{o} - \frac{ABS}{\varepsilon}\right)\left(A_{o} - \frac{ABS}{\varepsilon}\right)$$

While the intercept is giving ΔH values, ΔS values can be obtained from the slope of the plot shown in Fig. 3.

Entropies of formation were lowest for monoanthracene complexes, along with diarylmethanes and (where determined) diarylethanes. The ΔS and ΔH values of the complexes are given in Table 2. The obtained results reveal that the CT complex formation process is exothermic and spontaneous.

The thermodynamic constants, ΔH , ΔS and equilibrium constants can be calculated from the slopes and the intercept of the EDA complexes of chloranil with anthracene compounds are given in Table 2. The slope and the intercept values were calculated from the experiments, which were used 1:1 ratio of the concentration of acceptor to the concentration of donor groups.

 $K_{\text{(calc.)}}$ (at 21 °C) values of the complexes of monoanthracene compounds with chloranil are about 1.1 and values of $K_{\text{(calc.)}}$ at for dianthracene compounds (n=3-5) are around 2 which is about double of the mono anthracene compounds. The value for di(9-anthryl)methane is 1.58 which is intermediate. Similiar results were obtained for charge



Fig. 3. Van't Hoff plot of anthracene series compounds–chloranil complex at the different temperatures (ANH: M1, MEA: M2, DAM: 1, DAR: 3, DAB: 4, DAP: 5).

transfer complexes of carbazole, ethylcarbazole and 1,*n*dicarbazolylalkanes with some acceptors [22]. There is an agreement between the trends in $K_{(calc.)}$ and K_{BH} values for the EDA complexes of anthracene with chloranil except for di(9-anthryl)methane, for which K_{BH} is relatively high.

The thermodynamic constants, ΔH , ΔS of mono anthracene compounds and di(9-anthryl)methane are more negative than dianthracene compounds. There is a good agreement with the literature values for the ΔH , ΔS values of anthracene compound which are -2.7 ± 0.3 kcal/mol and -8.7 ± 0.8 cal/° mol [23], compared to $\Delta S = -8.4$ and $\Delta H = -2.40$ kcal/mol reported in here.

As a result, these dimeric compounds were prepared to model the behavior of polymeric systems related to polyvinylanthracenes. In pendant types of polymeric systems (for instance, polyvinylanthracenes, polyvinylcarbazole [24], polypyrole [25]), photoconductivity depends on the spacing of the pendant units in the polymer backbone. Conduction in polymers involves removal of one electron from one of the pendent groups, followed by hopping of the remaining positive hole from group to group through the polymer. The effects of distance and orientation between anthracene groups was investigated by synthesizing these 1,*n*-di(9-anthryl)alkanes (when n = 1-5). From the X-ray crystal structure [21], the 1,3-di(9-anthryl)propane is most similar to the poly(9-vinylanthracene) due to comparable separation of the anthracene groups.

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References

- [1] J.M. Pearson, Pure Appl. Chem. 49 (1977) 463.
- [2] US Patent 4,043,812, 1977.
- [3] A.R. Blythe, Electrical Properties of Polymer, New York, 1979.
- [4] J. Mort, G. Pfister, Electrical Properties of Polymer, Wiley-Int, New York, 1982.
- [5] P.J. Reucroft, Electrical Properties of Polymer, Technomic Pub. Co. Inc., Westport, 1972.
- [6] G. Briebleb, Elektronen-Donator Acceptor Komplexe, Springer-Verlag, Berlin, 1961.

- [7] R. Foster, Organic Charge-Transfer Complexes, Academic Press, New York, 1969.
- [8] L.J. Andrews, R.M. Keefer, Molecular Complexes in Organic. Chemistry, Holden Day, San Francisco, 1969.
- [9] J.M. Masnovi, J.K. Kochi, E.F. Hilinski, P.M. Rentzepis, J. Am. Chem. Soc. 108 (1986) 1126.
- [10] R. Foster, Molecular Association, Academic Press, New York, 1975.
- [11] B. Chakraborty, A.S. Mukherjee, B.K. Seal, Spectrochim. Acta Part A 57 (2001) 223–229.
- [12] F. Yakuphanoglu, M. Arslan, Opt. Mater. 27 (2004) 29-37.
- [13] F. Yakuphanoglu, M. Arslan, Solid State Commun. 132 (2004) 229–234.
- [14] F. Yakuphanoglu, M. Arslan, S.Z. Yıldız, Opt. Mater. 27 (2005) 1153–1158.
- [15] F. Yakuphanoglu, M. Arslan, M. Küçükislamoğlu, M. Zengin, Sol. Energy 79 (2005) 96–100.

- [16] R. Mandal, S.C. Lahiri, J. Indian Chem. Soc. 76 (1999) 347-349.
- [17] H.D. Becker, K. Anderson, J. Org. Chem. 48 (1983) 4542-4549.
- [18] R. Job, Advanced Physicochemical Experiment, Pitman, London, 1964.
- [19] H.A. Benesi, J.H. Hildebrand, J. Am. Chem. Soc. 71 (1949) 2703.
- [20] R.S. Mulliken, J. Am. Chem. Soc. 74 (1952) 811-824.
- [21] M. Arslan, Ph.D. Dissertation, Cleveland State University, Cleveland, 1998.
- [22] G.J. haderski, Z. Chen, R.B. Krafcik, J. Masnovi, R.J. Baker, R.L.R. Towns, J. Phys. Chem. B 104 (2000) 2242–2250.
- [23] M. Lotfi, R.M.G. Roberts, Tetrahedron 35 (1979) 2123.
- [24] K. Abe, S. Haibara, Y. Itoh, S. Senoh, Macromol. Chem. 186 (1985) 1505.
- [25] T.A. Ezquerra, J. Ruhe, G. Wegner, Chem. Phys. Lett. 144 (1988) 194.