

EDA Complexes of 2,3-Dichloro-1,4-naphthoquinone with Some Substituted Anilines

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Summary. Electron donor-acceptor (EDA) complexes of several substituted anilines with the π -acceptor 2,3-dichloro-1,4-naphthoquinone (DCINQ) in chloroform, dichloromethane, and 1,2-dichloroethane were studied by a spectrophotometric method. Experimental data has been shown to confirm the 1:2 stoichiometry of the acceptor-donor in spite of the apparent linearity of the *Benesi-Hildebrand* plot for a 1:1 complex. The calculated values of oscillator strengths, transition moments, and thermodynamic parameters confirms the 1:2 (A:D) stoichiometry of the complexes. The formation constants and molar absorptivities for these AD₂ complexes have been evaluated. The stoichiometry was unaffected by the variation of the temperature over a small interval and also by the change in polarity of the solvent. The order of the donor strength followed the sequence: *N*-benzylaniline > *p*-chloroaniline > *m*-chloroaniline > *o*-chloroaniline.

Keywords. EDA complex; CT-Complexes; 2,3-Dichloro-1,4-naphthoquinone (DCINQ); Spectrophotometric; Thermodynamic.

Introduction

The formation of electron donor-acceptor (EDA) or charge-transfer (CT) complexes has long been recognized as an important phenomenon in many chemical processes [1]. Recently, EDA complexes have gained much importance due to their potential non-linear optical activity [2] and other properties [3–8]. 1,4-Naphthoquinone is an π -acceptor with an electron affinity of 0.57 eV [9] and forms weak complexes with aromatic hydrocarbons [9] and amines [10]. It is well established that the electron affinity of the naphthoquinone acceptor is enhanced by the introduction of electron withdrawing substituents like chloro-, nitro-, and cyano-, *etc.*, in the 1,4-naphthoquinone π -system [9]. Earlier studies on polymethylbenzene-

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iodine complexes [11–15] have shown that the increased methylation of the donor molecule increases the strength of the donor resulting in the formation of stronger complexes that show a red shift of the charge-transfer absorption band [16]. The effect of substituents on the position of λ_{\max} is attributed to the ability of the substituents to interact with the π -orbitals of the benzene molecule [17–19]. For this reason the electron accepting ability of 2,3-dichloro-1,4-naphthoquinone (*DCINQ*) with some aromatic anilines (electron donors) in three different solvents, *viz.*, chloroform, dichloromethane, and 1,2-dichloroethane at four different temperatures was studied.

The *Rose-Drago* method of treating the experimental data was used for the evaluation of the formation constant (K_c) and the molar extinction coefficient (ϵ_λ), whereas *van't Hoff* plots were used for the calculation of the thermodynamic parameters. The values of oscillator strength (f) and transition moment (μ_{EN}) of each complex were evaluated using the approximate equations due to *H. Tsubumora* and *R. Lang* [20]. The change in the thermodynamic as well as spectroscopic properties of the complexes in different solvents was also studied.

Results and Discussion

The *DCINQ* acceptor forms charge-transfer complexes or molecular complexes of different colours with different aromatic anilines in all three solvents studied, *viz.*, chloroform, dichloromethane, and 1,2-dichloroethane. The typical charge-transfer spectra of the complex formed between *DCINQ* and *m*-chloroaniline in 1,2-dichloroethane at various concentrations of the donor at 35°C are shown in Fig. 1. In all systems studied, the absorption maxima were found on the shorter wavelength side

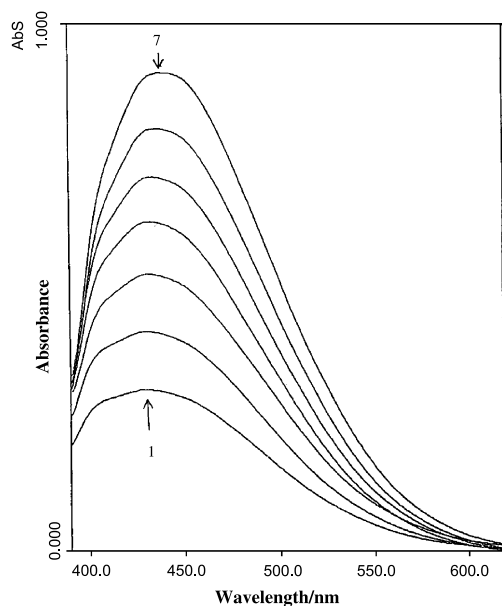


Fig. 1. Absorption spectra of 2,3-dichloro-1,4-naphthoquinone-*m*-chloroaniline complex at various concentrations of the donor in 1,2-dichloroethane at 35°C

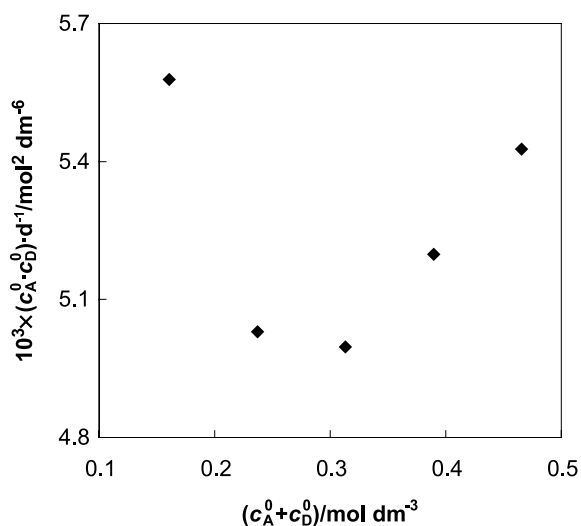
Table 1. The absorption maxima of the charge-transfer complexes of 2,3-dichloro-1,4-naphthoquinone with different aromatic anilines in different solvents

Donor	Solvent	λ_{\max}/nm	$\nu_{\max} \cdot 10^{-14}/\text{sec}^{-1}$	$\bar{\nu}_{\max}/\text{cm}^{-1}$
<i>N</i> -benzylaniline	chloroform	454.0	6.6079	22462
	dichloromethane	448.0	6.6964	21528
	1,2-dichloroethane	452.0	6.6371	22411
<i>p</i> -chloroaniline	chloroform	450.2	6.6637	22212
	dichloromethane	448.0	6.0241	20080
	1,2-dichloroethane	442.3	6.7827	22609
<i>m</i> -chloroaniline	chloroform	433.6	6.9188	23062
	dichloromethane	432.2	6.9412	23137
	1,2-dichloroethane	426.4	7.0356	23452
<i>o</i> -chloroaniline	chloroform	426.7	7.0307	23435
	dichloromethane	428.0	7.0093	23364
	1,2-dichloroethane	432.9	6.9300	23100

of the visible region. The charge-transfer bands were found to be broad in nature and are unaffected by the change of solvent except that there was a shift in the wavelength of maximum absorption by ± 2 nm. The spectra showed that for each system there is a well-defined maximum without shoulders.

The λ_{\max} , ν_{\max} , and $\bar{\nu}_{\max}$ values of all the complexes of DCINQ with different aromatic anilines in three different solvents are given in Table 1.

The experimental data shows that an increase in temperature has little effect on the absorption maximum for each of the complexes studied indicating that the variation of temperature does not alter the stoichiometry of the complexes.

**Fig. 2.** Rose-Drago plot for 2,3-dichloro-1,4-naphthoquinone-*p*-chloroaniline complex in 1,2-dichloroethane at 30°C for 1:1 stoichiometry

Formation Constants and Molar Extinction Coefficients

The absorbance values d of the complexes obtained experimentally were used to calculate the molar absorptivities and formation constants using the *Rose-Drago* equation [21]. This equation, unlike the *Benesi-Hildebrand* equation [11], does not depend on the experimental condition that one of the two component species (preferably donor) should be in large excess. So its concentration is virtually

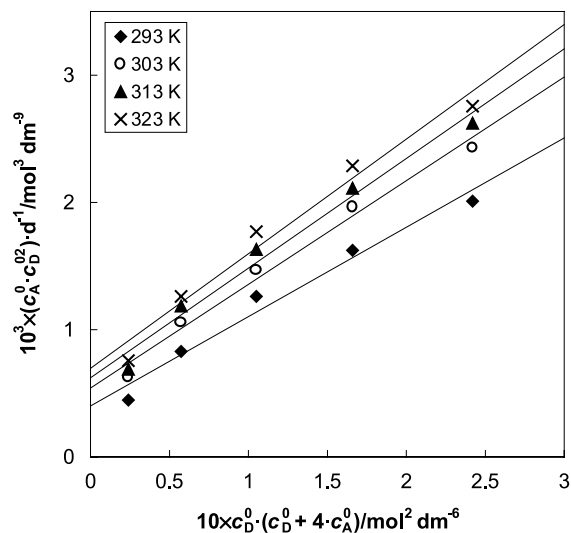


Fig. 3. *Rose-Drago* plot for 2,3-dichloro-1,4-naphthoquinone-*p*-chloroaniline complex in 1,2-dichloroethane for 1:2 (A:D) stoichiometry

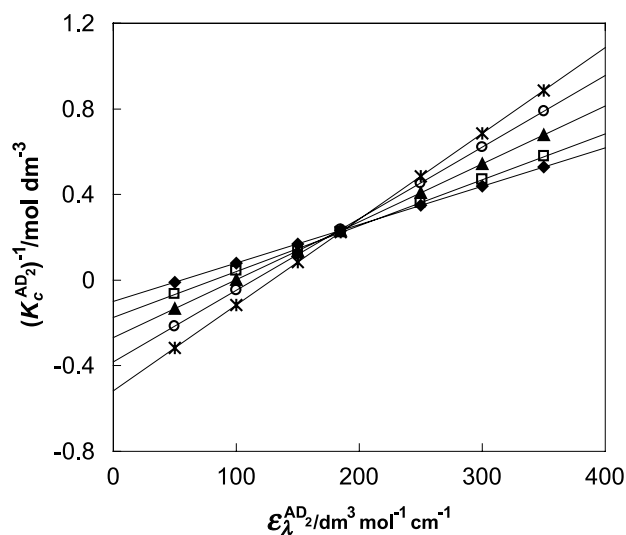


Fig. 4. *Rose-Drago* intersection plot for 2,3-dichloro-1,4-naphthoquinone-*o*-chloroaniline complex in 1,2-dichloroethane for 1:2 (A:D) stoichiometry at 40°C

Table 2. Formation constants ($K_c^{AD_2}$) and molar extinction coefficients ($\epsilon_\lambda^{AD_2}$) of 2,3-dichloro-1,4-naphthoquinone with different aromatic anilines in different solvents at different temperatures

Donor	Solvent	Temp/ $^{\circ}$ C	$K_c^{AD_2}/\text{dm}^3 \text{ mol}^{-1}$	$\epsilon_\lambda^{AD_2}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
<i>N</i> -benzylaniline	chloroform	20	87.22 ± 3.61	114.25 ± 2.71
		30	75.27 ± 2.88	112.20 ± 2.82
		40	74.01 ± 2.98	102.88 ± 2.71
		50	72.94 ± 2.85	102.60 ± 2.73
	dichloromethane	20	80.62 ± 3.44	100.88 ± 2.60
		25	71.79 ± 3.24	102.45 ± 2.51
		30	68.61 ± 2.95	099.56 ± 2.50
		35	63.79 ± 3.06	098.82 ± 2.42
	1,2-dichloroethane	20	82.09 ± 3.36	103.37 ± 4.61
		30	81.95 ± 3.79	096.27 ± 4.80
		40	78.18 ± 2.91	091.95 ± 4.52
		50	77.40 ± 3.25	084.58 ± 4.30
<i>p</i> -chloroaniline	chloroform	20	13.61 ± 0.01	140.97 ± 4.72
		30	13.57 ± 0.01	129.18 ± 4.60
		40	13.55 ± 0.01	118.86 ± 4.50
		50	13.36 ± 0.01	113.98 ± 4.41
	dichloromethane	20	13.51 ± 0.01	132.85 ± 6.01
		25	13.14 ± 0.01	132.20 ± 6.12
		30	12.88 ± 0.01	120.37 ± 5.81
		35	12.54 ± 0.01	119.94 ± 5.01
	1,2-dichloroethane	20	17.53 ± 0.01	142.60 ± 4.61
		30	15.00 ± 0.01	122.92 ± 4.81
		40	13.79 ± 0.01	115.29 ± 4.50
		50	12.89 ± 0.01	111.24 ± 4.31
<i>m</i> -chloroaniline	chloroform	20	5.41 ± 0.01	210.42 ± 5.21
		30	5.19 ± 0.01	184.39 ± 5.02
		40	4.99 ± 0.01	182.14 ± 5.12
		50	4.77 ± 0.01	177.86 ± 5.31
	dichloromethane	20	4.98 ± 0.01	196.68 ± 6.02
		25	4.83 ± 0.01	196.53 ± 6.11
		30	4.77 ± 0.01	183.20 ± 5.81
		35	4.36 ± 0.01	176.35 ± 5.02
	1,2-dichloroethane	20	4.39 ± 0.01	194.53 ± 5.11
		30	4.33 ± 0.01	192.55 ± 5.32
		40	4.11 ± 0.01	190.69 ± 5.01
		50	4.09 ± 0.01	185.70 ± 5.40
<i>o</i> -chloroaniline	chloroform	20	4.90 ± 0.01	207.77 ± 5.51
		30	4.76 ± 0.01	193.28 ± 5.80
		40	4.67 ± 0.01	184.63 ± 4.91
		50	4.36 ± 0.01	179.98 ± 4.90
	dichloromethane	20	5.24 ± 0.01	185.68 ± 5.01
		25	4.91 ± 0.01	179.31 ± 5.62
		30	4.31 ± 0.01	178.38 ± 5.31

(continued)

Table 2 (continued)

Donor	Solvent	Temp/°C	$K_c^{AD_2}/\text{dm}^3 \text{ mol}^{-1}$	$\varepsilon_\lambda^{AD_2}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
		35	4.28 ± 0.01	174.79 ± 5.11
	1,2-dichloroethane	20	7.20 ± 0.01	192.19 ± 5.01
		30	5.71 ± 0.01	200.64 ± 5.22
		40	3.77 ± 0.01	185.03 ± 7.11
		50	2.29 ± 0.01	158.33 ± 4.01

unaltered on complexation. Although the *Rose-Drago* method appears to be complicated, it is versatile in its general nature of applicability.

A typical *Rose-Drago* plot, *i.e.*, the plot of $c_A^0 \cdot c_D^0/d$ vs. $(c_A^0 + c_D^0)$ for 1:1 stoichiometry for one of the systems studied at 25°C is shown in Fig. 2. The experimental data pairs were found to be completely scattered or did not conform to a straight line, suggesting that the stoichiometry of the complexes is different from 1:1. However, when the experimental data were fit into the equation for the 1:2 (A:D) stoichiometry [22], straight line plots were obtained. Figure 3 may be regarded as a *Rose-Drago* linear plot for the 1:2 (A:D) stoichiometry. These systems show good linear relationships for the 1:2 (A:D) stoichiometry. A typical *Rose-Drago* intersection plot for one of the systems studied is shown in Fig. 4. Though the formation constant $K_C^{AD_2}$ and the molar extinction coefficient $\varepsilon_\lambda^{AD_2}$ of the charge-transfer complexes can be calculated by the use of *Rose-Drago* linear plots for the 1:2 (A:D) stoichiometry, we have estimated these parameters for all the systems by using the *Rose-Drago* intersection plots. This method resulted in more reliable results [21] in spite of its tedious nature. The values thus obtained along with the associated errors are given in Table 2. The errors in $\varepsilon_\lambda^{AD_2}$ were found to be less than 5%. The λ_{max} for each system remains almost constant irrespective of the change in temperature and solvent. This indicates that the 1:2 (A:D) stoichiometry of the complexes is not affected by the change in temperature or solvent.

The wave number ($\bar{\nu}_{\text{max}}$) values of charge transfer complexes of DCINQ decrease with an increase in the donor strength indicating stronger interaction [23, 24]. Though aniline or *N*-alkylanilines act as 'n' donors using the lone pair of electrons present on the nitrogen atom, these electrons make the $-\text{NH}_2$ or $-\text{NR}_2$ group a $n\pi$ -donor towards the $-\text{C}_6\text{H}_5$ group in an intramolecular $n\pi$ - $a\pi$ action [25]. In case of π -electrons not conjugated with the ring, the lone pair of electrons will still be almost like a π -island. It takes part in intermolecular charge-transfer as π -donor [26]. The new absorption bands may, therefore, be regarded as due to $b\pi$ - $a\pi$ -complexes.

The stabilities of these complexes increase with increasing electron-releasing ability of the substituents. Further, the substituents on the 1,4-naphthoquinone molecule affect the acceptor strength in such a way that the intermolecular interaction involves aromatic π -electrons of the donor rather than the lone pair of electrons. Thus, introduction of some substituents like $-\text{Cl}$ on 1,4-naphthoquinone enhances the strength of the acceptor and hence leads to the larger values of formation constants.

The relative magnitudes of $K_c^{AD_2}$ at the lowest temperature of the measurement were used to measure the relative strength of donor. On the basis of magnitudes of formation constants in chloroform at the lowest temperature of measurement, the relative order of donor strength was found to be: N-benzylaniline > *p*-chloroaniline > *m*-chloroaniline > *o*-chloroaniline. Of the four donors, N-benzylaniline is the strongest. Out of the remaining three donors, the strength of *p*-chloroaniline is greater than those of the remaining two. At the meta position electron density is less, and hence it should be lowest in the donor strength. But in case of

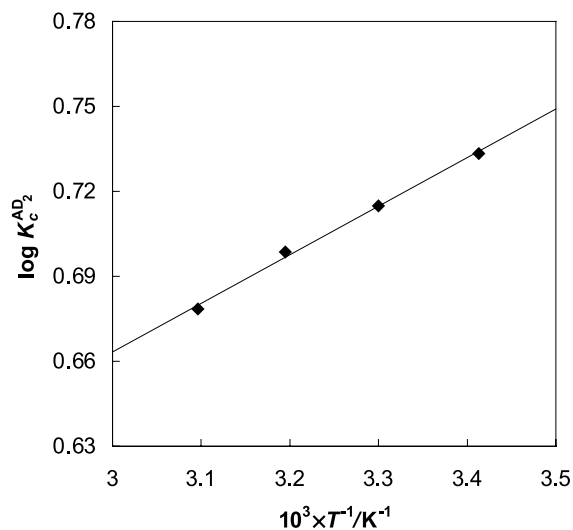


Fig. 5. Van't Hoff plot for 2,3-dichloro-1,4-naphthoquinone-*m*-chloroaniline complex in chloroform

Table 3. Thermodynamic parameters of the complexes formed between 2,3-dichloro-1,4-naphthoquinone and different aromatic anilines in different solvents at 293 K

Donor	Solvent	$-AH/kJ mol^{-1}$	$-\Delta S/J K^{-1} mol^{-1}$	$-\Delta G/kJ mol^{-1}$
N-benzylaniline	CHCl ₃	04.42 ± 0.004	-22.07 ± 0.52	10.89 ± 0.68
	CH ₂ Cl ₂	11.24 ± 0.004	01.86 ± 0.36	10.69 ± 0.53
	C ₂ H ₄ Cl ₂	01.75 ± 0.004	-30.66 ± 0.90	10.74 ± 0.55
<i>p</i> -chloroaniline	CHCl ₃	00.45 ± 0.004	-20.17 ± 1.32	6.36 ± 0.41
	CH ₂ Cl ₂	15.13 ± 0.008	29.98 ± 2.21	6.34 ± 0.36
	C ₂ H ₄ Cl ₂	07.96 ± 0.008	03.34 ± 0.12	6.98 ± 0.41
<i>m</i> -chloroaniline	CHCl ₃	3.28 ± 0.004	-2.84 ± 0.08	4.11 ± 0.18
	CH ₂ Cl ₂	3.99 ± 0.004	1.32 ± 0.05	3.60 ± 0.21
	C ₂ H ₄ Cl ₂	3.14 ± 0.004	-2.46 ± 0.07	3.91 ± 0.25
<i>o</i> -chloroaniline	CHCl ₃	02.87 ± 0.004	-03.42 ± 0.07	3.87 ± 0.17
	CH ₂ Cl ₂	13.88 ± 0.010	34.04 ± 2.19	3.90 ± 0.16
	C ₂ H ₄ Cl ₂	06.04 ± 0.008	07.04 ± 0.64	3.97 ± 0.19

o-chloroaniline, because of steric hindrance, the electron donating capacity becomes less and hence the donor strength of *o*-chloroaniline turns out to be the least.

The formation of charge-transfer complexes is temperature dependent. Hence the variation of formation constants with temperature may be used to determine the thermodynamic parameters of the complexes. These thermodynamic parameters may be obtained from the familiar *van't Hoff* plots assuming ΔH as constant over a range of temperatures. A typical *van't Hoff* plot for one of the systems studied is shown in Fig. 5. The thermodynamic parameters evaluated by the use of such plots are summarized in Table 3. The negative *Gibbs* energies show that the complex formation is thermodynamically favoured, while the negative entropy indicates a decrease in the degree of freedom of the components upon complexation. *Andrews* and *Keefe* [27] had earlier demonstrated that ΔH and ΔS generally become more and more negative as the stability constant for molecular complexation increases. As the binding between donor and acceptor becomes stronger, ΔH would be expected to have higher negative values. The high negative value of ΔH and the larger values of formation constants are an indicator to the strength of binding between donor and acceptor and the high stability of the resultant charge-transfer complexes.

Calculation of Spectroscopic Parameters of the Charge-transfer Complexes

The values of oscillator strength (f) which is a measure of integrated intensity of the CT-band [28] and transition moment (μ_{EN}), were calculated by using the approximate equations due to *H. Tsubumora* and *R. Lang* [20] given in Eqs. (1) and (2), where $\varepsilon_{\lambda}^{\text{max}}$ is the molar extinction coefficient of the CT-complex at the wavelength of maximum absorption and $\Delta\bar{\nu}_{0.5}$ is the half band-width in wave number units. The values of ' f ' and ' μ_{EN} ' thus obtained are given in Table 4.

$$f \approx 4.32 \times 10^{-9} \times \varepsilon_{\lambda}^{\text{max}} \times \Delta\bar{\nu}_{0.5} \quad (1)$$

$$\mu_{\text{EN}}(\text{Debyes}) \approx 0.0958 \left(\frac{\varepsilon_{\lambda}^{\text{max}} \times \Delta\bar{\nu}_{0.5}}{\bar{\nu}_{\text{max}}} \right)^{1/2} \quad (2)$$

It is evident from these equations that the values of these parameters depend purely on $\varepsilon_{\lambda}^{\text{max}}$ and $\Delta\bar{\nu}_{0.5}$. The near constancy of these two parameters is an additional support for our findings with respect to the stoichiometry of all the complexes of *DCINQ* studied.

The relation between charge-transfer energy ($h\nu_{\text{CT}}$) of the lowest intermolecular CT-band and the ionization potentials of donors with a certain acceptor has been given by *McConnel et al.* [29] in the form of Eq. (3), where W is the dissociation energy of the CT-excited state, E^{A} is the electron affinity of the acceptor and I^{D} is the ionization potential of the donor.

$$h\nu_{\text{CT}} = I^{\text{D}} - E^{\text{A}} - W \quad (3)$$

Though this relationship gives a linear plot when $h\nu_{\text{CT}}$ vs. I^{D} is plotted, which may some times be used to determine the ionization potentials of very weak donors,

Table 4. Spectroscopic parameters of 2,3-dichloro-1,4-naphthoquinone with various aromatic anilines in different solvents at different temperatures

Donor	Solvent	Temp/°C	$\bar{\nu}_{\max}/\text{cm}^{-1}$	$\Delta\bar{\nu}_{0.5}/\text{cm}^{-1}$	f	μ_{EN}/D
<i>N</i> -benzylaniline	CHCl ₃	20	22027.92	61849.41	0.03052	1.76
		30	22222.22	60030.29	0.02909	1.67
		40	22627.81	56656.80	0.02746	1.61
		50	23001.63	53594.43	0.02375	1.48
	CH ₂ Cl ₂	20	22324.16	60740.45	0.02647	1.59
		25	21345.13	78397.8	0.03469	1.86
		30	21374.57	78434.35	0.03373	1.83
		35	21119.29	82606.12	0.03526	1.88
	C ₂ H ₄ Cl ₂	20	22124.54	60250.49	0.02690	1.61
		30	22430.08	56654.7	0.02356	1.49
		40	22425.13	59584.4	0.02367	1.50
		50	22681.41	56648.41	0.02069	1.39
<i>p</i> -chloroaniline	CHCl ₃	20	22242.65	58401.29	0.03556	1.84
		30	22299.82	59605.92	0.03326	1.78
		40	22066.00	64863.11	0.03330	1.79
		50	22239.21	63804.88	0.03142	1.73
	CH ₂ Cl ₂	20	19905.06	55111.9	0.03163	1.84
		25	20044.92	55630.42	0.03177	1.84
		30	20152.35	54768.93	0.02848	1.73
		35	20209.79	54104.27	0.02827	1.72
	C ₂ H ₄ Cl ₂	20	22213.35	62313.23	0.03838	1.92
		30	22626.26	58430.77	0.03103	1.71
		40	22822.17	56452.14	0.02836	1.62
		50	22799.31	57019.51	0.02740	1.60
<i>m</i> -chloroaniline	CHCl ₃	20	23199.20	66726.93	0.06065	2.36
		30	23219.49	71802.27	0.05719	2.28
		40	22803.03	77958.87	0.06134	2.39
		50	23035.76	76663.86	0.05890	2.33
	CH ₂ Cl ₂	20	23148.11	73351.21	0.06164	2.38
		25	23152.52	73682.52	0.06129	2.37
		30	23098.96	74769.07	0.06159	2.38
		35	23151.91	73685.02	0.05911	2.33
	C ₂ H ₄ Cl ₂	20	23417.76	64990.76	0.05522	2.24
		30	23429.71	67499.97	0.05730	2.28
		40	23530.40	68375.19	0.05411	2.21
		50	23429.97	71382.13	0.05438	2.22
<i>o</i> -chloroaniline	CHCl ₃	20	23045.3	62226.27	0.05585	2.27
		30	23259.24	60713.21	0.05069	2.15
		40	23646.08	57905.86	0.04618	2.04
		50	23795.78	58565.92	0.04553	2.02
	CH ₂ Cl ₂	20	23397.10	47461.10	0.05088	2.15
		25	23313.01	63816.46	0.05020	2.14

(continued)

Table 4 (continued)

Donor	Solvent	Temp/ $^{\circ}\text{C}$	$\bar{\nu}_{\text{max}}/\text{cm}^{-1}$	$\Delta\bar{\nu}_{0.5}/\text{cm}^{-1}$	f	μ_{EN}/D
		30	23311.62	65824.24	0.05072	2.15
		35	23436.45	65768.75	0.05161	2.16
	$\text{C}_2\text{H}_4\text{Cl}_2$	20	23649.58	57840.73	0.04802	2.08
		30	23606.06	61636.66	0.05342	2.19
		40	23453.12	65353.23	0.05224	2.17
		50	21796.59	110126.50	0.07532	2.69

Table 5. Ionization potentials (I^{D}) of donors, dissociation energies (W) of the charge-transfer excited states, and $h\nu_{\text{CT}}$ of the 2,3-dichloro-1,4-naphthoquinone with aromatic anilines in different solvents

Donor	Solvent	I^{D}/eV	$h\nu_{\text{CT}}/\text{eV}$	W/eV
N-benzylaniline	chloroform	8.6226	2.7906	4.8520
	dichloromethane	8.4812	2.6746	4.8266
	1,2-dichloroethane	8.6150	2.7843	4.8507
<i>p</i> -chloroaniline	chloroform	8.5848	2.7596	4.8452
	dichloromethane	8.2612	2.4942	4.7870
	1,2-dichloroethane	8.6449	2.8088	4.8560
<i>m</i> -chloroaniline	chloroform	8.7137	2.8652	4.8684
	dichloromethane	8.7250	2.8745	4.8705
	1,2-dichloroethane	8.7727	2.9136	4.8790
<i>o</i> -chloroaniline	chloroform	8.7702	2.9115	4.8786
	dichloromethane	8.7594	2.9027	4.8767
	1,2-dichloroethane	8.7193	2.8698	4.8694

the linearity is questionable over a wide range of I^{D} values [27]. Since the value of E^{A} for DC1NQ is 0.9 eV, by using Eq. (3), the dissociation energies (W) of the charge-transfer excited state were calculated and are given in Table 5.

It was found that the plot of $h\nu_{\text{CT}}$ vs. I^{D} is linear for complexes of iodine [29], 1,3,5-trinitrobenzene [30], and chloranil [31] for a number of donors. It may be considered as independent of donors [27]. A more detailed consideration of the energetic of charge-transfer processes has resulted in an alternative relationship (Eq. (4)) between $h\nu_{\text{CT}}$ and I^{D} for complexes with a given acceptor by *Matsen et al.* [30], where 'C' and ' β ' are approximately constants.

$$h\nu_{\text{CT}} = I^{\text{D}} - C + \frac{2\beta^2}{(I^{\text{D}} - C)} \quad (4)$$

Mulliken and *Person* [26] have identified 'C' with the sum of vertical electron affinity of the acceptor and the attraction energy between the component molecules in the charge-transfer process and β with the resonance integral between electron donating and accepting orbitals while the equation is one of a parabola rather than a straight line, a plot of $h\nu_{\text{CT}}$ vs. I^{D} is expected to give a straight line when $(I^{\text{D}} - C)$ is greater than β [32]. Figure 6 is such a plot for the acceptor studied with different

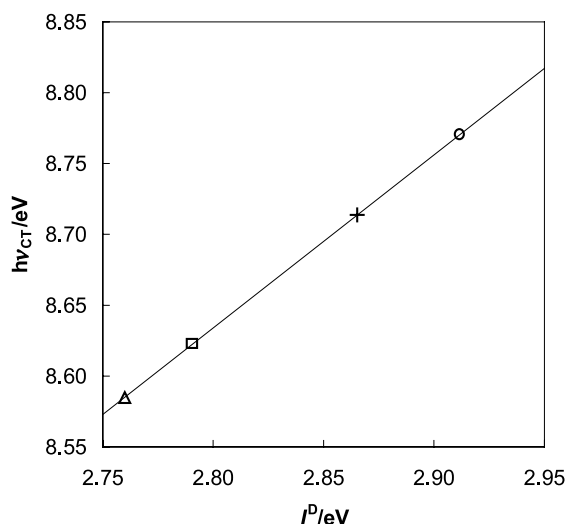


Fig. 6. The plot of W vs. I^D of aromatic aniline donors for 2,3-dichloro-1,4-naphthoquinone in chloroform (Δ : p -chloroaniline, \square : N -benzylaniline, +: o -chloroaniline, \circ : m -chloroaniline)

donors, which shows a linear relationship. The lower value of the slope is the characteristic of higher resonance stabilization [26].

Effect of Solvent on the Formation of CT-complexes

The electronic absorption spectra of the intermolecular charge-transfer complexes of some aromatic anilines with DCINQ in different solvents, *viz.*, chloroform, dichloromethane, and 1,2-dichloroethane with dielectric constants 4.7, 8.9, and 10.37, respectively, have been recorded. The formation constants $K_c^{AD_2}$, molar extinction coefficients, $\epsilon_\lambda^{AD_2}$, and thermodynamic parameters of these complexes were also determined in all three solvents used. In the present investigations, no definite conclusions can be drawn for the dependence of formation constants $K_c^{AD_2}$ and thermodynamic parameters of these complexes on the solvent.

The results of the present study in different solvents shows that $K_c^{AD_2}$ values and thermodynamic parameters are not of the same order in all the solvents studied. There seems to be a strong influence of the solvent on the complexes chosen, [33, 34] although, its nature could not be positively identified.

Conclusions

Molecular complexes of DCINQ with various aromatic anilines were studied spectrophotometrically in three different solvents, *viz.*, chloroform, dichloromethane, and 1,2-dichloroethane at four different temperatures. All these complexes show a new broad charge-transfer band in the visible region of the electromagnetic spectrum. All the donors are known to form 1:2 (A:D) complexes with the acceptor and their stoichiometry was unaffected by variation of temperature over an interval and independent of the solvents used. The formation constants $K_c^{AD_2}$ and molar extinction coefficients $\epsilon_\lambda^{AD_2}$ of all the complexes were evaluated by the *Rose-Drago*

intersection plots. The calculated thermodynamic and spectroscopic parameters suggest that the stoichiometry of the complexes is 1:2 (A:D). The change in the thermodynamic as well as spectroscopic properties of the complexes in different solvents is assumed to be due to the solvent interaction with *DCINQ*. Based on the values of the formation constant, the order of donor strength in chloroform at the lowest temperature of measurement was found to be: *N*-benzylaniline > *p*-chloroaniline > *m*-chloroaniline > *o*-chloroaniline.

Experimental

Out of different donors used in the present investigations, *o*- and *m*-chloroanilines and *N*-benzylaniline were Ranbaxy samples whereas *p*-chloroaniline was a Fluka sample. All the donors except *p*-chloroaniline were dried over caustic potash and distilled twice just before use under reduced pressure, whereas *p*-chloroaniline was purified by recrystallization using pet. ether (40–60°C). Melting point of the compound was found to be 70°C (uncorrected) which agrees well with the reported value [35]. Spectral grade chloroform, dichloromethane, and 1,2-dichloroethane (Ranbaxy) were used as solvents without further purification. The *DCINQ* (Fluka) was purified by recrystallization twice from chloroform to get bright yellow flakes (mp 196°C, uncorrected).

Fresh stock solutions were always prepared by directly weighing the required quantities of the respective compounds in 25 cm³ volumetric flasks and then the solutions were made up to the mark with the solvent. Freshly prepared solutions were always used for absorbance measurements. As far as possible, the solutions were protected against direct light. Desired volumes of acceptor and donor solutions were pipetted out into 5 cm³ volumetric flasks and made up to the mark with the solvent. The electronic absorption spectra of such solutions were recorded by using a "CARRY-50" Bio UV-VIS Spectrophotometer at a low scan speed. 'A' grade glasswares were used in all the spectral measurements in the present study. A matched pair of teflon stoppered air tight quartz cuvettes were used throughout the studies. Peltier accessory was used to maintain the temperature at a desired value. The uncertainty in temperature of the solution was ±0.1°C.

In the complexes of *DCINQ*, the charge transfer bands appeared on the shorter wavelength side of the visible region with all the donors studied. The band maxima in all these cases were rather close to the wavelength of maximum absorption of the acceptor. Hence, instead of pure solvent, acceptor solution of the same concentration as it is in the complex solution, was used in the reference beam to avoid the absorption due to the acceptor in the region where the complex absorbs. All the spectral measurements of absorbance *d* were made by keeping the acceptor concentration constant and the concentration of the donor was varied, always maintaining the condition that $c_D^0 \gg c_A^0$, where c_A^0 and c_D^0 are the initial concentrations of acceptor and donor, respectively. Sufficient time was allowed for the solution to attain thermal equilibrium before each spectrum was recorded.

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