Charge-Transfer Interactions of Nicotine with Chloranil : Solvent Effects UV-Visible Spectrophotometric Study

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UV-visible spectrophotometric studies on the interaction of nicotine with chloranil in cyclohexane, dioxane, benzene, chloroform and dichloromethane solutions at 25 °C demonstrate the formation of charge-transfer (CT) complexes. A new broad band begins to grow in time on the longer wavelength side of the characteristic absorption bands of the constituents. At equilibrium, the new band position depends on the polarity of the solvent used. In EtOH, MeOH and DMSO solutions, a new absorption spectra are immediately formed after mixing. The position of the new spectra is not affected by the solvent polarity. The solvation of the CT-complex immediately causes complete ionization of the neutral complex. It has been found that acetone acts as intermediate between the non-ionizing and ionizing solvents in which absorptions corresponding to the ions are observed simultaneously with the intermolecular CT-absorption. The stability constants and the molar absorptivities of the complexes formed have been calculated assuming the formation of 1 : 1 complexes. Experimental results indicate that the stability constant of the complex formed and its type (neutral or ionic) depends greatly on the dielectric constant of the solvent used.

INTRODUCTION

Charge-transfer (CT) complexes play an essential part in many fundamental mechanisms in the field of biology.[1] The formation of such associations between carcinogenic substances and acceptors has been observed.[2]

There is increasing interest in nicotine for its biochemical and pharmacological[4,5] effects. Nicotine metabolites are organspecific and local carcinogens.[6] Interactions between nicotine and drugs have been the subject of many investigations.[5,7]

A considerable amount of work[8a] has been carried out on interactions with the well-known organic electron acceptor chloranil. This molecule was chosen as a model for the biological quinones.[9-13] Interactions between nicotine and chloranil have not been reported earlier. In continuation of our interest in the CT-interactions of nicotine with organic electron acceptors,[14] it would be interesting to study the interactions of nicotine with chloranil in organic solvents of different dielectric constants with the purpose of clarifying the solvent effects on the complexation process.

Materials and Methods

Nicotine (BDH) was used as such. Chloranil (Aldrich) was recrystallized repeatedly from benzene, to give yellow platelets; m.p. 289 °C. Spectral grade quality solvents (BDH or E. Merck) were used after fresh distillation. The electronic absorption data of nicotine and chloranil in the solvents used are given in Tables I and II.

The calculated volumes of nicotine (5.0×10^{-2} M) and chloranil (4.0×10^{-3} M) were transferred to a 10 ml dark flask and the volume was filled up to the mark with the spectral grade quality solvent. The initial concentration of nicotine was varied in the range of $(0.62—33.64) \times 10^{-3}$ M while chloranil concentration was varied in the range of $(0.09—17.92) \times 10^{-5}$ M. All solutions were freshly prepared each day, and their absorbances as well as those of their mixtures were measured within 16 hours. Most operations were performed in an air-conditioned room ($\sim 20\,°C$) in subdued light. At the beginning of the measurements of a set of solutions, the spectra of pure compounds were taken to detect all changes.

Spectrophotometric measurements were made on a Shimadzu UV-200 S double beam spectrophotometer, using a rectangular cell of 1 cm pathlength against solvent as blank. Absorbances were measured at fixed wavelengths to minimize errors arising from the steepness of absorption spectra. The absorption band of the complex formed between nicotine and chloranil was detected at a wavelength longer than those of individual pure components at concentrations identical to that in the mixture. The absorbances were measured within ~ 10 minutes after placing the cell in a thermostated cell holder for equilibrium. The accuracy of the measurement was ± 0.01 absorbance unit.

RESULTS

Interaction of nicotine with chloranil was investigated in organic solvents of different dielectric constants, in the range of 2.023 to 46.62 $\varepsilon_{\text{vacuum}—1}$, at 25 °C.

The Behaviour in Solvents of Low and Medium Dielectric Constants

For nicotine-chloranil mixtures in cyclohexane, dioxane, benzene, chloroform and dichloromethane, a new broad assymetrical band begins to grow in time on the longer wavelength side of the characteristic absorption bands of the constituents. The apparent band heigh and position depend on the time after mixing. Under the experimental conditions, the time needed to stabilize the new spectrum (i.e. the time required to reach a steady state of the interaction) ranges from 5 to 9 hours depending on the dielectric constant of the solvent used. At equilibrium, the absorbance of the new band increases in value with the increase in nicotine content in the initial mixture (Figure 1). The new band position (λ_{max}) is very sensitive to the solvent polarity (Table I and Figure 2), so that the appearance of this new longer wavelength band is attributed to the formation of a CT-complex[8b] between nicotine and chloranil in the solvent used.

The stability constant (K_c^{NC}) of the complex formed due to the CT-interaction (1) is defined using the Benesi-Hildebrand equation (2):[15]

$$N + C \rightleftharpoons NC \tag{1}$$
$$\text{(neutral CT-complex)}$$

$$\frac{[C]_0}{A_\lambda^{NC}} = \frac{1}{K_c^{NC} \cdot \varepsilon_\lambda^{NC}} \cdot \frac{1}{[N]_0} + \frac{1}{\varepsilon_\lambda^{NC}} \tag{2}$$
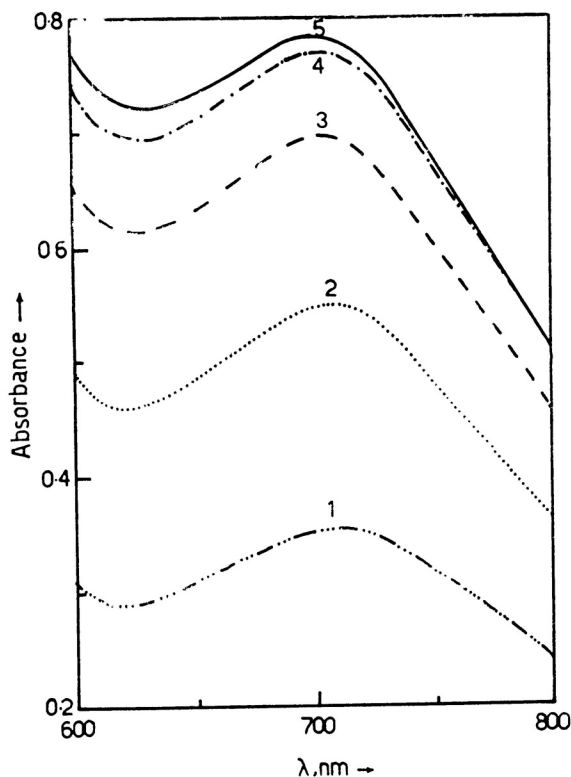
Figure 1. The electronic absorption spectra of nicotine-chloranil mixtures in di-chloromethane after 15 hours of mixing at 25 °C. [chloranil] $= 1.8 \times 10^{-3}$ M, [nicotine] $\times 10^{-2}$ M: (1) 0.50; (2) 1.00; (3) 2.00; (4) 2.50 and (5) 3.00.

where NC is the non-ionic CT-complex formed, $[N]_o$ and $[C]_o$ are the initial concentrations of nicotine (N) and chloranil (C), respectively. ε_λ^{NC} and A_λ^{NC} are the molar absorptivity and the absorbance of the complex at the wave-length of measurement λ. For a series of solutions of constant $[C]_o$ and varying $[N]_o$, at equilibrium, a plot of $[C]_o/A_\lambda^{NC}$ against $[N]_o^{-1}$ should be linear. The intercept of the line with the ordinate is $(\varepsilon_\lambda^{NC})^{-1}$ and the gradient is equal to $(\varepsilon_\lambda^{NC} \cdot K_c^{NC})^{-1}$, so that K_c^{NC} and ε_λ^{NC} can be evaluated. Plots of Eq. (2) for nicotine-chloranil mixtures are represented in Figure 3 while K_c^{NC} and ε_λ^{NC} values are given in Table I. In nicotine-chloranil mixtures in cyclo-hexane and benzene solutions a thich brown viscous fluid is formed with time. Elemental analyses data of the dry fluid product separated in benzene solution at 25 °C are: found: C, 46.93; H, 3.20; N, 6.77. $C_{10}H_{14}N_2 : C_6O_2Cl_4$ requires C, 47.06; H, 3.43; N, 6.86%.

The Behaviour in Solvents of High Dielectric Constants

Nicotine-chloranil mixtures in acetone, ethanol, methanol and dimethyl-sulphoxide new strong absorption spectra immediately form after mixing (Figure 4 and Table II). The position of the new spectra is not affected by

TABLE I

Absorption maxima $(\lambda_{max})^a$, *molar extinction coefficients* $(\varepsilon_{max})^a$ *and stability constants* $(K_c^{NC})^a$ *of nicotine (N), chloranil (C) and nicotine-chloranil (NC) complex in non-ionizing solvents at 25 °C*

Solvent $\left(\begin{array}{c}\text{Dielectric constant}\\ \varepsilon_{vacuum}-1\end{array}\right)^c$	Nicotine $\lambda^N_{max}\ (\varepsilon^N_{max})$		Chloranil $\lambda^C_{max}\ (\varepsilon^C_{max})$		NC-Complex $\lambda^{NC}_{max}\ (\varepsilon^{NC}_{max})$	K
Cyclohexane (2.023)	252 *sh* (2410) 257 (2756) 262 (2676) 267 *sh* (2134)		282 *sh* (2835) 291 (3303) 370 (181)		580(—)	—
Dioxane (2.209)	247 *sh* (2167) 257 (2857) 261 (2827) 268 *sh* (2153)		278 *sh* (12695) 285 (14499) 320 *sh* (1849)		644(704)	34.51 ± 0.61
Benzene (2.284)	— —		284 (15137) 330 *sh* (2363)		702(—)	—
Chloroform (4.806)	246 *sh* (4016) 257 (5293) 263 (5402) 268 *sh* (4177)		285 *sh* (16391) 294 (22588) 362 (286)		690(581)	44.46 ± 0.98
Dichloromethan (9.08)	253 *sh* (1807) 258 (2023) 263 (2068) 268 *sh* (1606)		284 *sh* (17391) 292 (24457) 374 (257)		708(592)	99.15 ± 2.04

[a] λ_{max} in nm; ε_{max} in cm^{-1} M^{-1}; K_c^{NC} in M^{-1}.

[b] Values listed are the means from three runs made for each system after 15 hours of mixing the components.

[c] *CRC Handbook of Chemistry and Physics* 61st Ed. (1980—1981) (CRC Press, Inc.).
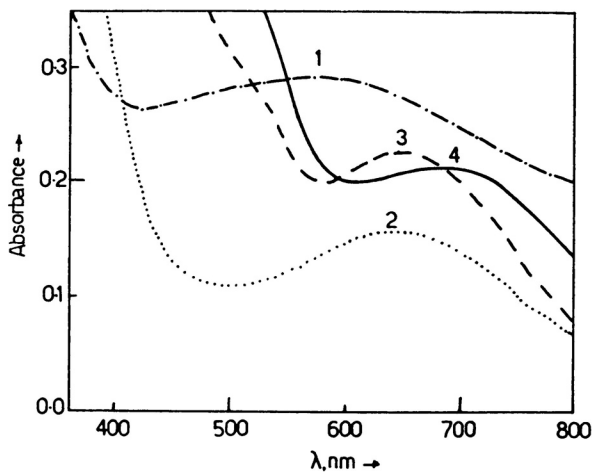

Figure 2. The electronic absorption spectra of nicotine (2.0×10^{-2} M) + chloranil (8.8×10^{-4} M) after 15 hours of mixing at 25 °C. Solvent composition: (1) pure cyclohexane, (2) 1 : 1 (v/v) mixtures of cyclohexane and dioxane, (3) 1 : 1 (v/v) mixtures of cyclohexane and chloroform and (4) 1 : 1 (v/v) mixtures of cyclohexane and dichloromethane.
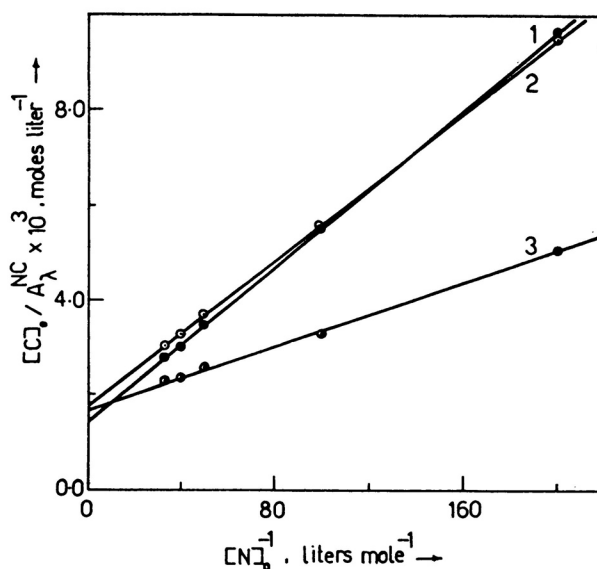
Figure 3. Plots of $[C]_o/A_\lambda^{NC}$ *versus* $[N]_o^{-1}$ for solutions containing fixed [chloranil] and different [nicotine] at 25 °C. Solvents: (1) dioxane; (2) $CHCl_3$ and (3) CH_2Cl_2.

the solvent polarity. This spectrum is that of the chloranil anion, *cf.* Discussion. When the dielectric constant of the solvent is reduced by adding CCl_4, the absorptions due to the ionic species diminish (Figure 5). The absorption spectra slowly change in time where the chloranil anion spectrum reverts to the spectrum of chloranil. The stoichiometry of the complex (N_nC_c),

$$nN + cC \rightleftharpoons N_nC_c \tag{3}$$

a complex with complete CT in
the ground state (ionic-complex)

was determined applying Eq. (4).[8c]

$$A_\lambda = K_c \cdot \varepsilon_\lambda [N]^n [C]^c \tag{4}$$

where A_λ and ε_λ are the absorbance and the molar absorptivity, respectively, of the complex at wavelength λ, and K_c is the stability constant. A plot of A_λ *versus* concentration of one component, that of the other being kept constant, on log paper, proved that the complex has the 1 : 1 composition.

Thus, the initial stability constant K_c^{NC} of the ionic complex formed is defined by applying the normal equilibrium method. For equilibrium (5),

$$N + C \rightleftharpoons NC \tag{5}$$

(ion-pair complex)

the results obtained by application of Eq. (2) are presented in Figure 6 while K_c^{NC} and ε_λ^{NC} values are given in Table II.

In all solvents used (non-ionizing or ionizing), it has been proved impossible to isolate a solid from the solutions by evaporation under a low pressure,
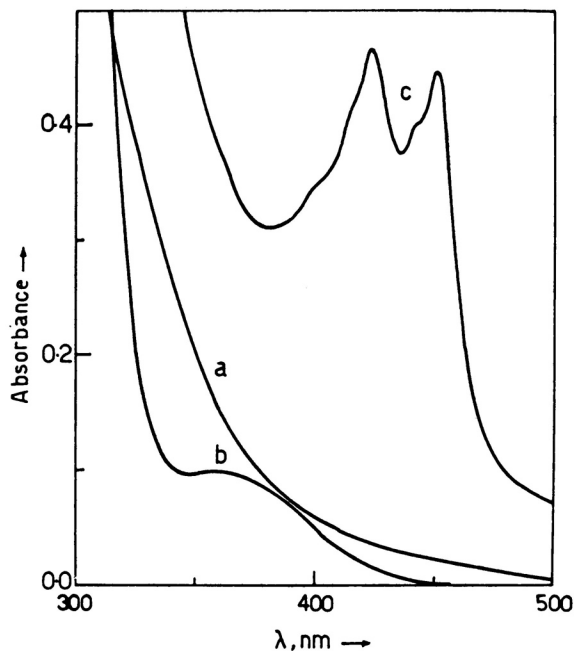
Figure 4. The electronic absorption spectra in ethanol at 25 °C. (a) nicotine (1.2 × × 10^{-2} M), (b) chloranil (3.6 × 10^{-4} M), (c) nicotine (1.2 × 10^{-2} M) + chloranil 3.6 × × 10^{-4} M).
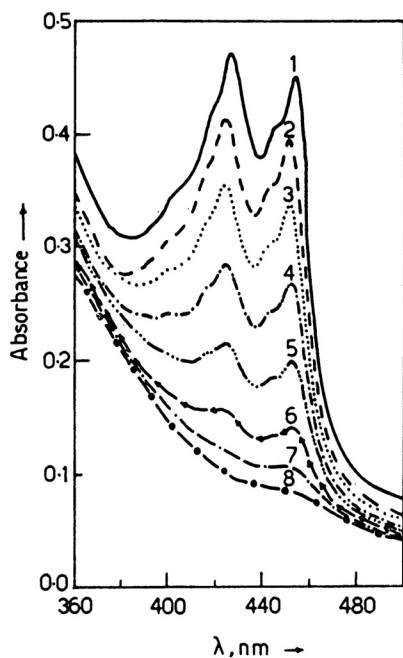

Figure 5. The electronic absorption spectra of nicotine (1.0 × 10^{-2} M) + chloranil (4.0 × 10^{-4} M) in EtOH—CCl_4 solution mixtures at 25 °C. The solutions contain: (1) 0.0, (2) 10.0, (3) 20.0, (4) 30.0, (5) 40.0, (6) 50.0, (7) 60.0 and (8) 80.0% (v/v) CCl_4.

TABLE II

Absorption maxima (λ_{max})[a], molar extinction coefficients (ε_{max})[a] and initial stability constants (K_c^{NC})[a] of nicotine (N), chloranil (C) and nicotine-chloranil (NC) complex in ionizing solvents at 25°C

Solvent (Dielectric constant) ε_{vacuum}—1	Nicotine λ^N_{max} (ε^N_{max})	Chloranil	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	K_c^{NC}	ε^{NC}_{max}
Acetone (20.70)		360 sh (368)	—	—	418	438sh	445	675	—	—
EtOH (24.30)	251 sh (2227) 257 (2761) 262 (2979) 268 sh (2228)	279 sh (13134) 287 (14671) 362 sh (243)	402sh	418sh	424	445sh	451	—	35.4	4255
MeOH (33.62)	250 sh (4614) 258 (5823) 262 (6325) 267 sh (4685)	287 (12665) 262 (281)	402sh	418sh	425	445sh	452	—	56.7	1667
DMSO (46.62)	266 sh (3804)	282 (12299) 356 (1604)	—	—	421	441sh	449	—	91.5	6993

[a] λ_{max} in nm; ε_{max} in cm^{-1} M^{-1}; K_c^{NC} in M^{-1}.
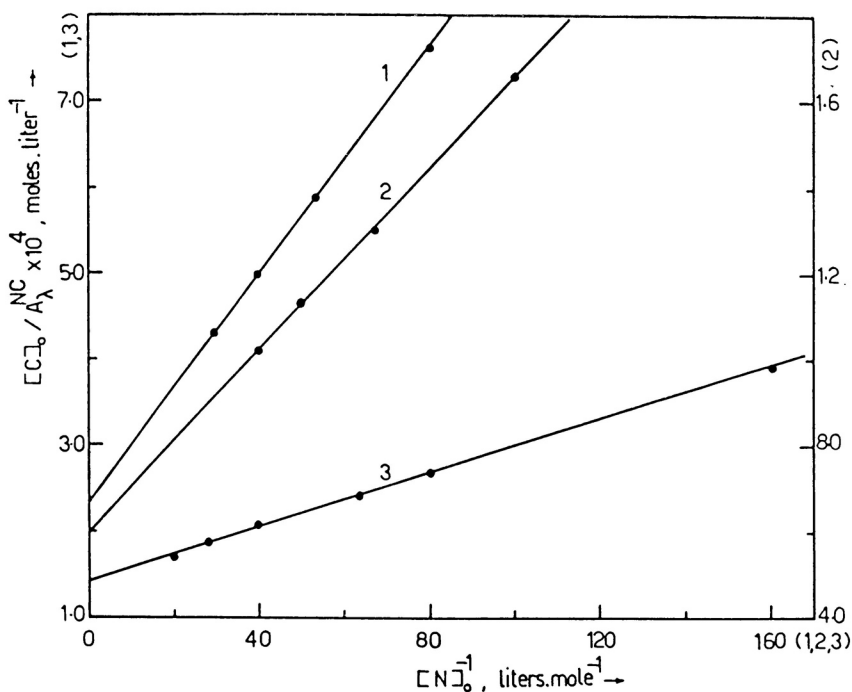
Figure 6. Plots of $[C]_o/A_\lambda^{NC}$ *versus* $[N]_o^{-1}$ for solutions containing fixed [chloranil] and different [nicotine] at 25 °C. Solvents: (1) EtOH; (2) MeOH and (3) DMSO.

as one could only evaporate down to a thick brown viscous fluid but no further.

DISCUSSION

The ground states of most organic CT-complexes involve very little transfer of charge when the complexes exist in solution in a solvent of low ionizing power. In such solutions the complexed species exist almost entirely as isolated complexed donor-acceptor pairs. If a solvent of high ionizing power is chosen, ionization of the essentially non-ionic complex may occur. The driving force is the energy of solvation of the ions formed.[16,17] Many CT-complexes which involve relatively strong donors and acceptors show this behaviour.[18-28]

Several studies[10,11,29] show that in solvents of high ionizing power the major absorption band of chloranil is red-shifted on complexing, a phenomenon particularly noticeable in strong donors.[10] The shift of the absorption is the spectrum of the negative ion. The resultant spectrum is, therefore, due to contributions to the spectrum from both neutral and ionized forms.

Spectral studies of solutions of mixtures of nicotine and chloranil in non-ionizing (cyclohexane, dioxane, benzene, chloroform and dichloromethane) and ionizing (acetone, EtOH, MeOH and DMSO) solvents have revealed some interesting changes.

On adding nicotine to chloranil in pure cyclohexane solution, a new single broad maximum occures at 580 nm. This new asymmetrical maximum is slow in developing. In 1 : 1 (v/v) initial mixtures of cyclohexane and one of the solvents: dioxane, chloroform or dichloromethane, the new band position at equilibrium (580 nm in pure cyclohexane) is shifted to 642, 650 or 682 nm, respectively, depending on the polarity of the medium (Figure 2). This has been taken as evidence supporting the assignment of this band to intermolecular CT transitions.[8b] For nicotine-chloranil mixtures in pure dioxane, benzene, chloroform and dichloromethane solutions, the same behaviour was observed as in pure cyclohexane solutions but the CT band position also changed in the range from 580 to 708 nm depending on the solvent used (Table I). At equilibrium, application of Eq. (2) gave linear slopes (Figure 3) which may be taken as an evidence of 1 : 1 complex formation. The results of elemental analysis of the thick brown viscous fluid obtained in benzene solution proved that the CT-complex has a 1 : 1 composition supporting the previous results.

In the non-ionizing solvents used, it is evident that the ability of nicotine to form CT-complexes with chloranil depends on the solvent dielectric constant. The values of K_c^{NC} decrease in the solvent order: $CH_2Cl_2 > CHCl_3 >$ dioxane (Table I).

In the ionizing solvents used (acetone, EtOH, MeOH and DMSO), the solvation of the CT-complex in nicotine-chloranil system immediately causes almost complete charge-transfer in the ground state, i. e. ionization of the complex. In ethanol solution, for example, the absorption band of the CT-complex is absent, but absorptions at 424, 451 nm which have been assigned to the semiquinone ion (II) derived from chloranil are observed (Figure 4).
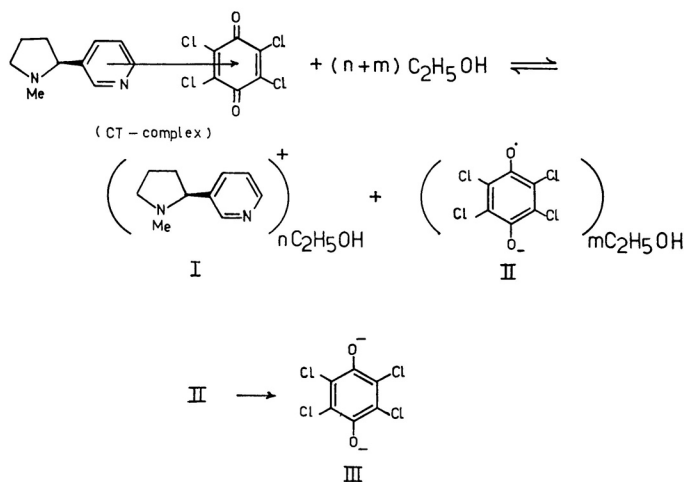
A support for this assignment is provided by:

i) the absorption position was not affected by the solvent polarity (Figure 5),

ii) the similarity of the absorption to that shown by the product obtained from the reaction of chloranil with sodium iodide in acetone.[21] It had pre-

viously been argued that this product is the sodium salt of the semiquinone ion.[22] Pott and Kommandeur[23] have suggested that this absorption is due to the dinegative ion (III) of chloranil formed by the disproportionation of II. Nevertheless, there seems little doubt that, initially, the nicotine-chloranil complex ionizes in solution to form N^+ and C^- species. Spectral studies on nicotine salts (tartarate and sulphate) indicate that the cation radical N^+ has no absorptions in the range from 400 to 750 nm.
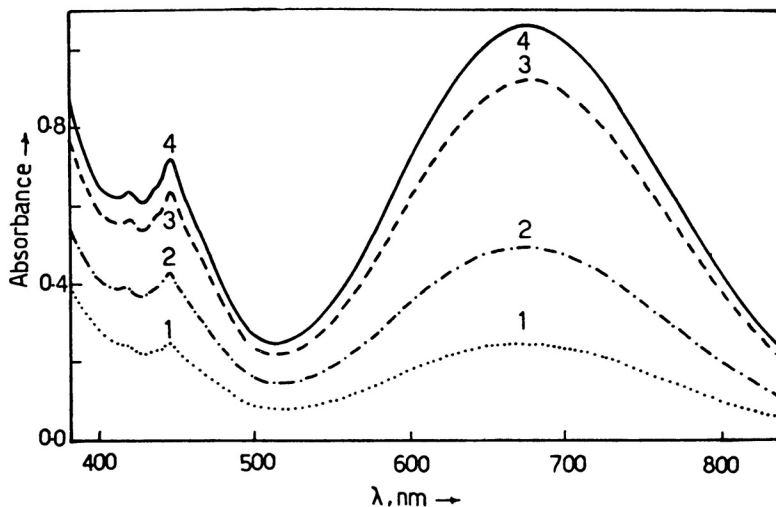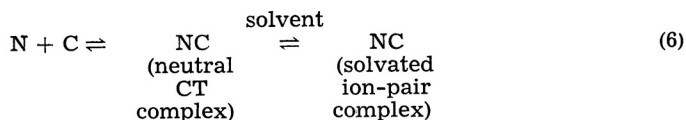

Figure 7. The electronic absorption spectra of nicotine-chloranil mixtures in acetone at 25 °C. [Chloranil] $= 6.8 \times 10^{-4}$ M, [nicotine] $\times 10^{-2}$ M: (1) 0.75; (2) 1.50; (3) 2.50; (4) 3.00.

Acetone appears to be a solvent intermediate between the non-ionizing and the ionizing solvents, in which absorptions corresponding to the species C^- (or C^{--}) are observed simultaneously with the intermolecular CT absorption (Figure 7). Here the equilibrium represented by Eq. (6) is fairly well balanced compared with the solvolytic action of the other ionizing solvents (ethanol, methanol and DMSO).

$$N + C \rightleftharpoons \underset{\substack{\text{(neutral} \\ \text{CT} \\ \text{complex)}}}{NC} \overset{\text{solvent}}{\rightleftharpoons} \underset{\substack{\text{(solvated} \\ \text{ion-pair} \\ \text{complex)}}}{NC} \qquad (6)$$

The equilibrium in acetone can be shifted more towards the CT-complex by reducing the temperature.

Application of Eq. (2) gives linear slopes (Figure 6) supporting the 1:1 complex formation. Experimental results indicate that the initial stability constant of the ion-pair complex depends on the solvent polarity, it decreases in the solvent order: DMSO > methanol > ethanol (Table II).

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SAŽETAK

Utjecaj otapala na prijenos naboja u interakciji nikotin-kloranil: UV/ViS spektrometrijska studija

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UV/ViS spektrometrijom proučavana je interakcija kloranila s nikotinom u nizu otapala (cikloheksan, dioksan, benzen, kloroform, diklorometan). Izveden je zaključak o nastanku kompleksa u kojima se zbiva prijenos naboja, s time da osobine tih kompleksa ovise o naravi otapala.