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Absorption Spectra of 2-Styryl-4-phenyl-thiazole Ethiodides in Organic Solvents of Varying Polarities and Determination of the Formation Constant of the Charge Transfer Complex Formed

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The electronic absorption spectra of some 2-styryl-4-phenyl-thiazole ethiodides are studied in organic solvents of different polarities. The shorter wavelength band appearing in the visible region is assigned to an intramolecular charge transfer (CT)-transition originating from the phenyl moiety to the positively charged hetero ring, while the longer wavelength one is due to an intermolecular CT-transition from the iodide ion to the 2-styryl-4-phenyl-thiazolinium cation. These assignments are based on the nature of the aldehydic residue and effects of solvent, concentration, and temperature on both the position and absorptivity of the CT complex-band. It is concluded that the CT complex formed will be highly solvated in *DMF*, *DMSO*, ethanol and methanol relative to in $CHCl_3$, dioxane and acetone. The formation constant of the CT complex in solutions of different polarities is determined at different temperatures. Furthermore, the thermodynamic parameters ΔH°, ΔG° and ΔS° for complex formation are calculated and discussed.

(Keywords: Charge transfer complexes; Solvent effects; Thermodynamic parameters; UV-Vis. spectra)

Absorptionsspektren von 2-Styryl-4-phenyl-thiazol-ethiodiden in verschiedenen Lösungsmitteln und Bestimmung der Bildungskonstanten der Charge-Transfer-Komplexe

Die Elektronenanregungsspektren einiger substituierter 2-Styryl-4-phenyl-thiazol-ethiodide wurden in einigen Lösungsmitteln unterschiedlicher Polarität untersucht. Die Absorption bei kürzerer Wellenlänge wird einem intramolekularen Charge-Transfer (CT)-Übergang zugeordnet, die langwellige Bande einem intermolekularen CT-Übergang (Jodid—organ. Kation). Die Diskussion erfolgt basierend auf Substitutions-, Lösungsmittel-, Konzentrations-, und Temperatur-Effekten. Die Komplexbildungskonstanten und die thermodynamischen Parameter ΔH°, ΔG° und ΔS° werden angegeben.

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Introduction

The structure and mechanism of solvolysis of styryl cyanine dyes are of interest for the study of the spectral sensitization. Furthermore, the application of styryl cyanine dyes as photosensitizers and desensitizers and many biological aspects[1–5] of these compounds prompted us to study of the absorption spectra of these compounds in different media.

The scanning of the literature reveals that the absorption data on styryl-4-phenyl-thiazole ethiodide derivatives were very scanty. Only *Kiprianov* and *Petrunkin*[6] published little informations concerning the ultraviolet spectra of cyanine dyes derived from 2-methyl-benzothiazole.

The present paper is devoted to the assignment of low energy transitions in the visible region of the electronic spectra of 2-styryl-4-phenyl-thiazole ethiodide derivatives and the solvent effect on these transitions. Furthermore, the work is extended to include the determination of the formation of the intermolecular charge transfer complex formed between the iodide ion and the *p*-hydroxy-styryl-cyanine cation at different temperatures in media of different polarities.

Experimental

Materials

2-Styryl-4-phenyl-thiazole ethiodides were prepared by condensing 2-methyl-4-phenyl-thiazole ethiodide with the corresponding aldehyde in presence of piperidine in similar manner to the method described by *Phillips*[7]. In most cases a resinous substance was obtained which was triturated successively with ether and light petroleum several times to give the solid product. 2-Methyl-4-phenyl-thiazole ethiodide was prepared according to the method described by *Hantzsch*[8]. The styryl cyanine derivatives obtained were crystallized several times from ethanol. The results of analysis of the solid products were in agreement with the composition of these compounds.

The organic solvents utilized in this investigation were all of spectroscopically pure grade. A. R. $NaClO_4$ and bidistilled water were used.

Solutions

$10^{-3}M$ stock solutions were prepared by dissolving the accurately weighted amount of the styryl cyanine compound in the appropriate volume of the solvent. More dilute solutions used for spectral measurements were obtained by accurate dilution.

For studying the behaviour in mixed organic solvents, the required volume of the stock solution was placed in a calibrated measuring flask followed by the required volume of the high polarity solvent. The mixture was then completed to the mark with the low polarity solvent.

Determination of Formation Constant

For determination of the formation constant of the intermolecular CT complex for compound **4**, a series of different concentrations of this compound in 60% ethanol-water mixture in presence of 0.1 *M*-$NaClO_4$ and in pure $CHCl_3$ were prepared. These solutions were placed for a sufficient time at the desired temperature in an ultrathermostat accurate to ± 0.5 °C. The visible spectra of these solutions in the charge transfer complex region were recorded rapidly. The temperatures used were 25, 30, 35 and 45 °C.

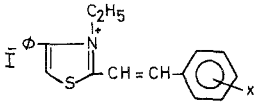
Apparatus

The spectra were recorded on a UNICAM S. P. 8000 Spectrophotometer within the 200-700 nm range using a 1 cm matched quartz cell.

Results and Discussion

Band Assignment

The compounds under consideration have the general structure



1 $X = H$
2 p-OCH_3
3 p-$N(CH_3)_2$
4 p-OH
5 o-OH
6 p-OH, m-OCH_3

The spectra of these compounds in ethanol (Fig. 1 and Table 1) can be considered as comprising of four absorption bands each except compounds **2** and **3** which are characterized by three bands only. The first in the range (210-225 nm) corresponds to the $\pi - \pi^*$ transitions of the benzenoid system ($'L_a$). The second band (250-276 nm) can be assigned to $\pi - \pi^*$ transitions within the thiazole ring[9]. The third band (350-408 nm) is highly influenced by substituents (X) and is attributed to a transition involving the whole molecule associated with intramolecular charge transfer. The intramolecular charge transfer is originated from the phenyl moiety as donor system to the delocalized molecular orbital on the 4-phenyl-thiazolinium cation as an acceptor center. However, the observed band red shift and intensity change run in more or less regular manner in accordance with the electron donating character of the substituent X and the ionisation energy of the phenyl system ($—C_6H_5 = 9.20$ ev; phenol $= 8.51$ ev; $—C_6H_5OCH_3 = 8.21$ ev and $C_6H_5\ N(CH_3)_2 = 7.12$ ev)[10]. This fact is substantiated by the linear relationship between λ_{max} and σ (The *Hammett* constant) as shown in Fig. 2. This behaviour supports the intramolecular CT nature of

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* These are the only values found in literature.

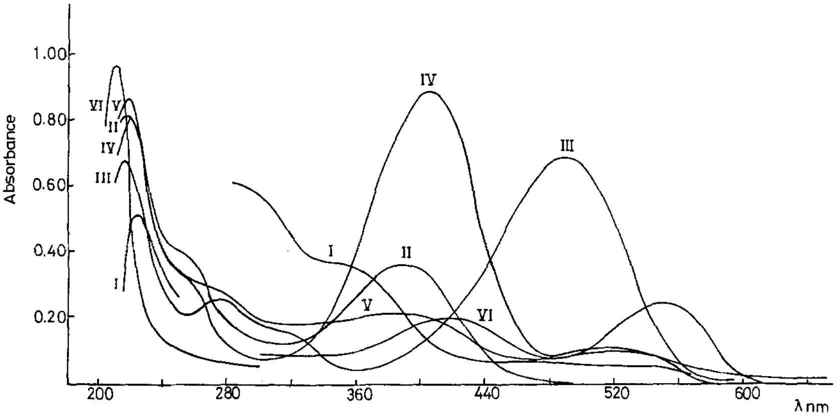


Fig. 1. Absorption spectra of $2.5 \times 10^{-5}\,M$ *X*-Styryl-4-phenyl thiazole ethiodides in absolute ethanol; compounds **1**—**6** (I—VI) [$1 \times 10^{-4}\,M$ used in the region 280-600 nm for **1** (I) and $1 \times 10^{-5}\,M$ used in the region 210-300 nm for **6** (VI)]

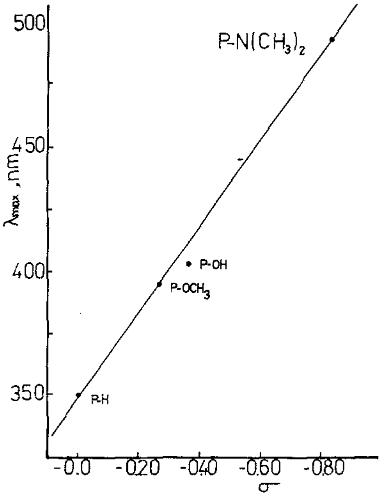
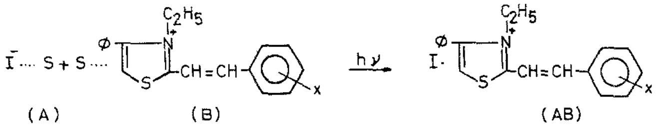


Fig. 2. Relationship between λ_{max} and the *Hammett* constant σ

this band. Furthermore, the breadth of the observed CT band, for example, in case of compounds **3** and **4** (Fig. 1) also suggests a CT transition, since such bands are characteristically broad[11].

In the light of the work of *Kosower*[12, 13] on the electronic spectra of quaternary heterocyclic iodides, one can assigne the fourth band located at longer wavelength (480-554 nm) in case of compounds **1**, **4**, **5** and **6** to an intermolecular charge transfer transition. The mechanism of this transition involves the interpenetration of the elctron cloud of the negatively charged iodide ion into the π-electron cloud of the positively charged heteroaromatic ring within an solvent sperated ion-pair leading to the formation of a charge transfer complex between these two ions. The mechanism of this CT transition can be represented by equation (1).



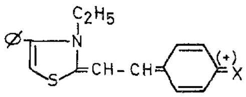
(1)

A support for this assignment is achieved from the dependence of the intensity of this band on concentration and temperature. The good straight line obtained on plotting the absorbance of this band against the dye concentration indicate that there is only one absorbing species which should be the CT complex. On the other hand, increasing the temperature from 25 to 45 °C, the molar absorptivity (ε) of this band (in case of compound **4**) in 60% ethanol-water mixtures is increased from 3,640 to 8,080 (Table 3); an increase in temperature will reduce the degrees of solvation of both the iodide and the 2-styryl-4-phenyl thiazolinium ions and consequently increase the concentration of the CT complex.

It is worthy to mention that the CT complex-band in case of compounds **2** and **3** can dissapear when it is submerged with the strong intramolecular CT band of these compounds (c.f. Fig. 1).

Solvent Effects on Intra and Intermolecular CT Bands

These two bands display apparent changes with solvent polarity. Generally the intramolecular CT band acquires a blue shift in its position in going from $CHCl_3 \rightarrow C_2H_5OH \rightarrow DMF = DMSO$ (Table 1). This shift can be explained on the principle that styryl cyanine dyes exist in the ground state predominately in a polar structure[7,14] with the charge partially at X.



Furthermore, the polarizability of the solvent molecules under investigations will be increase in the sequence[15] $CHCl_3 <$ ethanol $< DMF < DMSO$. Thus the blue shift observed can be mainly due to the high stabilization of the polar structure of the dye by polarization interaction forces. The polarization interaction will be established between the delocalized oscillator dipole of the styryl cyanine polar structure and the localized oscillator dipole of the solvent molecule. However, the blue shift observed in the position of the intramolecular CT band in ethanol relative to *DMF* or *DMSO* in case of compounds **1** and **2** can be attributed to an additional specific interactions probably to occur between the molecules of these compounds and that of these solvents.

Table 1. *Spectral bands obtained in organic solvents at 25 °C* (λ/nm. ε/g mol^{-1} cm^2)

Compound	Ethanol		$CHCl_3$		*DMF*		*DMSO*	
	λ_{max}	$\varepsilon_{max} \times 10^{-3}$	λ_{max}	$\varepsilon_{max} \times 10^{-3}$	λ_{max}	$\varepsilon_{max} \times 10^{-3}$	λ_{max}	$\varepsilon_{max} \times 10^{-3}$
1	225	21.20	—	—	—	—	—	—
	270	6.00	285	6.20	280	6.40	280	6.50
	350	3.60	360	4.15	355	4.80	355	4.40
	480	0.55	480	0.55	480	0.55	480	0.55
2	220	33.00	—	—	—	—	—	—
	255	sh	292	11.60	—	—	—	—
	390	14.40	400	22.80	393	28.40	394	21.60
3	220	33.50	244	24.00	—	—	—	—
	276	sh	278	sh	275	sh	275	19.00
	490	32.50	505	47.00	486	44.00	487	32.50
4	220	32.40	—	—	—	—	—	—
	250	sh	—	—	—	—	—	—
	404	35.40	414	28.80	401	23.80	402	34.40
	522	4.00	565	1.60	564	16.00	565	2.60
5	218	34.40	—	—	—	—	—	—
	265	12.00	—	—	—	—	—	—
	390	8.60	405	8.00	387	6.00	388	8.80
	525	3.60	565	1.20	580	6.60	577	3.40
6	210	9.80	—	—	—	—	—	—
	417	8.00	423	13.00	414	16.80	415	6.00
	554	9.800	580	1.00	577	32.00	580	23.60

On the other hand, the intermolecular CT complex-band belonging to compounds **4** and **6** exhibit a blue shift in its location as the *Z* value of the solvent is increased except in case of *DMF* or *DMSO* (Table 2 and Fig. 3). This can be considered as an evidence for the CT complex-transition of this band according to *Kosower*[12, 13].

The relationship between the energy of this band and *Kosower*'s *Z*-values of the solvents used is found to be linear only for the solvents

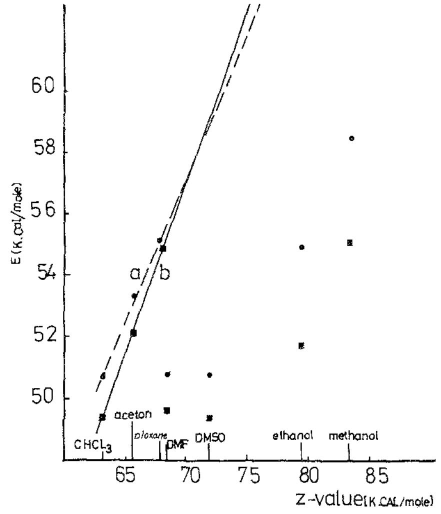


Fig. 3. Relationship between the CT complex energy and the Z-values at 25 °C; *a* compound **4** and *b* compound **6**

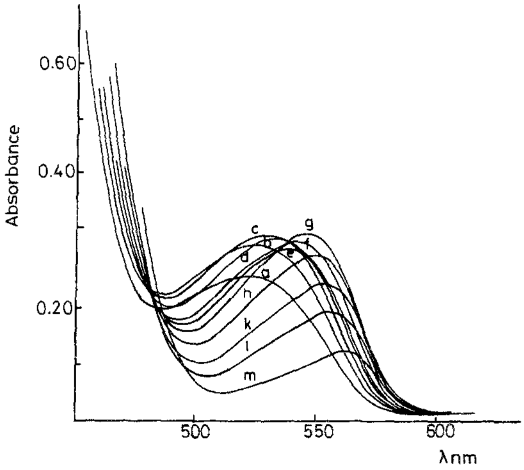


Fig. 4. CT complex transition of $1 \times 10^{-4}\,M$ **4** in $CHCl_3$-ethanol mixtures at 25 °C mole fraction of $CHCl_3$: *a* 0.0753; *b* 0.1548; *c* 0.2389; *d* 0.3281; *e* 0.4228; *f* 0.5235; *g* 0.6309; *h* 0.7456; *k* 0.8059; *l* 0.8552; *m* 1

Table 2. *Solvent effect on the complex* CT-*band of compounds* **4** *and* **6** *at 25 °C*

	Z-value	Compound **4**				Compound **6**			
Solvent	kcal/mol	λ_{max}	$E_{kcal/mol}$	$\varepsilon_{max} \times 10^{-3}$	f	λ_{max}	$E_{kcal/mol}$	$\varepsilon_{max} \times 10^{-3}$	f
Chloroform	63.20	565	50.68	1.60	0.0035	580	49.37	1.450	0.006
Acetone	65.70	535	53.25	1.50	0.0025	550	52.06	1.375	0.005
Dioxane	67.88	520	55.07	0.45	0.0028	522	54.86	0.625	0.003
DMF	68.50	564	50.77	31.20	0.078	577	49.63	32.000	0.097
DMSO	71.70	565	50.68	2.60	0.005	580	49.37	32.600	0.095
Ethanol	79.60	522	54.85	4.00	0.021	554	51.68	9.800	0.055
Methanol	83.60	490	58.43	2.00	0.012	520	55.07	4.060	0.030

Table 3. *The formation constant* (*K*) values, molar absorptivities (ε) *and thermodynamic function for the intermolecular* CT *complex of* **4** *in solutions of different polarities*

Solvent	*K*, 10^{-4}				ε, $\times 10^{-3}$				ΔH° kcal/mol	ΔS° cal/deg. 25 °C	$-\Delta G^\circ$ kcal/mol 25 °C
	25 °C	30 °C	35 °C	45 °C	25 °C	30 °C	35 °C	45 °C			
60% ethanol-water	12.2	14.66	20.17	25.42	3.344	4.555	5.17	8.08	7.11	0.40	6.99
$CHCl_3$	0.66	—	9.51	16.80	0.294	—	0.294	0.297	10.20	12.11	6.61

$CHCl_3$, acetone and dioxane, as shown in Figure 3. The points in case of *DMF*, *DMSO*, ethanol and methanol are far off the line, thus indicating a specific solvation of the CT-complex in these solvents.

The high degree of solvation of the CT complex in *DMF*, *DMSO*, ethanol and methanol relative to in $CHCl_3$, dioxane and acetone is confirmed by the high absorptivity or the high experimental oscillator strength (f) of the CT complex-band in the former solvents relative to in the latter ones (Table 2). Furthermore the stabilization of the CT complex by specific solvation is verified by investigating the spectra of compounds **4** and **6** in $CHCl_3$-ethanol mixtures. The spectra in these mixed solvents (Fig. 4), show a regular decrease in the extinction of the CT complex-band and its shift to red with increasing proportion of $CHCl_3$. The plot of the CT complex-transition energy shift $\Delta\bar{\nu}$ as a function of solvent dielectric constant $\left(\frac{D-1}{D+1}\right)$ (Ref.[16,17]) is a nonlinear relationship as shown in Fig. 5 indicating that the band shift is governed by other specific interactions besides the unspecific ones.

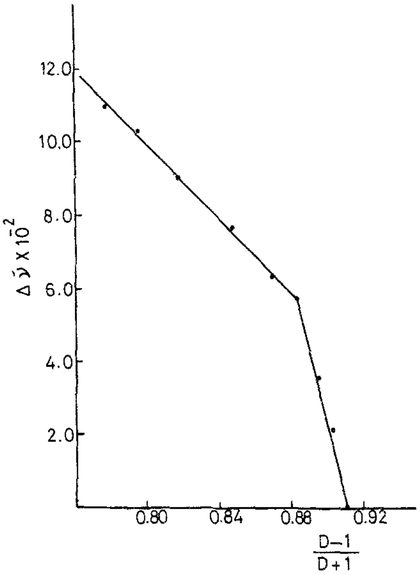


Fig. 5. Relationship between CT complex transition energy shift ($\Delta\nu$) and $(D-1)/(D+1)$ for compound **4** in $CHCl_3$-ethanol mixture at 25 °C

Formation Constant of the CT Complexes and Thermodynamic Parameters

The formation constant (K) and the molar absorptivity (ε_{AB}) of the intermolecular CT complex formed between the iodide ion (A) and the 3-ethyl-2-(4′-hydroxy-styryl)-4-phenylthiazolinium cation (B) (compound **4**) as indicated by equation (1) in 60% ethanol-water mixture and in pure $CHCl_3$ which is taken as representative example were determined at different temperatures in the range 25-45 °C (Table 3).

The equation used is that given in[18, 19]

$$\frac{L}{E_{AB}} = \frac{1}{K\,\varepsilon_{AB}} P + \frac{1}{\varepsilon_{AB}} \qquad (2)$$

$L = C_o^2/(2\,C_o - C_{AB})$ and $P = 1/(2\,C_o - C_{AB})$ for $C_{o_A} = C_{o_B} = C_o$; C_{o_A}, C_{o_B} represent the initial molar concentration of the A and B respectively; C_{AB} is the molar concentration of the CT complex formed (AB); C_o is the initial molar concentration of **4**. Furthermore E_{AB} is the absorbance due to the CT complex and is equal to $C_{AB}\,\varepsilon_{AB} = E - E_B - E_A$; E is the measured absorbance and E_B, E_A are the absorbances due to the species A, B at the selected wavelength respectively. Since, the iodide ion (A) absorb mainly in the near ultraviolet region[20] and the absorbance measurements were carried out at the λ_{max} of the CT complex, the measured absorbance is taken as equal to the absorbance due the CT complex throughout all calculations.

In order to obtain more accurate values of K and ε_{AB} equ. (2) is solved iteratively. Thus for different intial concentrations of compound **4**, L/E_{AB} and P were calculated first by assuming that $C_{AB} = 0$ and plotted one against the other and the required straight line was obtained. The method of least squares was used to define the best straight line through the experimental points, and from this line, tentative values of K and ε_{AB} were determined. Since K is larger, it become necessary to calculate the concentration of the CT complex for each initial concentration using these first values of K and ε_{AB}. This was made by making use of the following equation.

$$C_{AB} = 2\,C_o - \frac{\varepsilon_{AB}\,C_o^2}{E_{AB}} + \frac{1}{K}$$

Then, we revised the values of $\dfrac{L}{E_{AB}}$ and P accordingly to repeat the above process to obtain new values of K and ε_{AB} (second iteration). Repeating the same method of calculation, further iterations were made till constant values of K and ε_{AB} were obtained.

The linear relationships between $\dfrac{L}{E_{AB}}$ and P values obtained from the fourth iteration giving accurate values for K and ε_{AB} in 60% ethanol-water and in $CHCl_3$ at 25 °C are shown in Fig. 6. The K and ε_{AB} values of the intermolecular CT complex belonging to dye **4** in 60% ethanol-water mixture and in $CHCl_3$ at different temperatures are recorded in Table 3. It is evident that the CT complex is more stable in

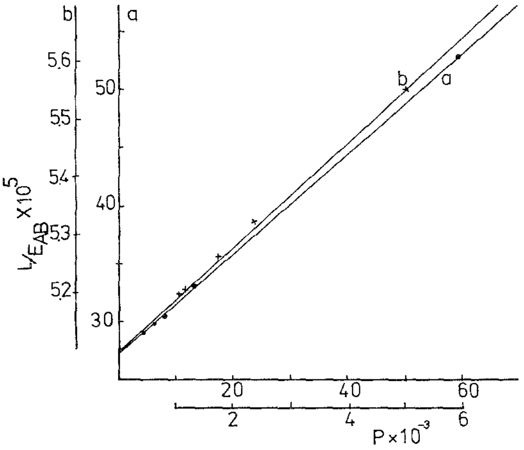


Fig. 6. Relationship between L/E_{AB} and P for compound 4 at 25 °C in: *a* 60% ethanol-water mixture; *b* $CHCl_3$

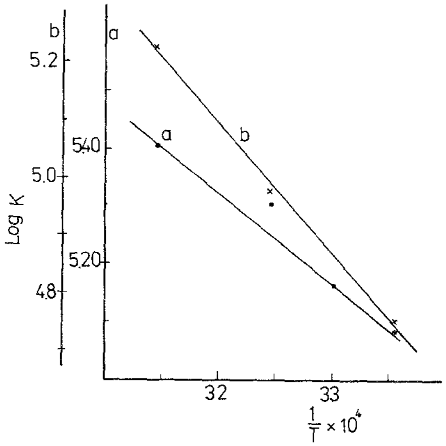


Fig. 7. *Vant-Hoff* plots for CT complex formation of compound 4 in: *a* 60% ethanol-water mixture; *b* $CHCl_3$

ethanol-water mixture than in $CHCl_3$ indicating the greater stabilization of the complex in the former solvent.

The thermodynamic parameters of this intermolecular CT complex formation ΔH°, ΔG° and ΔS° were calculated and the results are given in Table 3. ΔH° was dertermined from the slope of the *Vant-Hoff* plots (Fig. 7) using the least squares method. ΔG° and ΔS° were determined making use the equations $\Delta G^\circ = -RT \ln K$ and $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$.

Examination of the results shown in Table 3 indicate that ΔH° values are positive confirming the fact that rate determining step of CT complex formation is the desolvation of the separated ions which is endothermic. Furthermore, the ΔS° value is less in ethanol-water mixture relative to $CHCl_3$ indicating that the extent of solvation of the CT complex is higher in the former solvent.

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