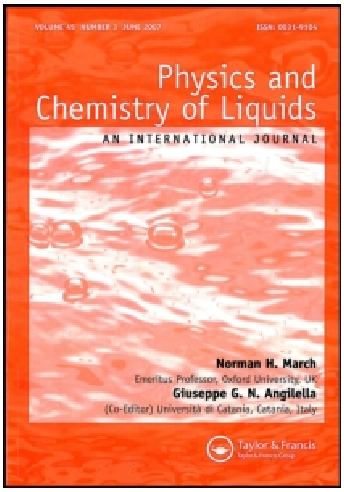

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Spectrophotometric studies of the formation of charge transfer complex of iron(III) with N,N′-bis(2-pyridylmethylidene)-1,2-diiminoethane di-Schiff base ligand in methanol

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The complex formation reaction between N,N′-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) di-Schiff base ligand as an electron donor and iron(III) chloride as an electron acceptor have been studied spectrophotometrically in methanol at 28°C. The values of equilibrium constants, K and molar absorptivities, ε were obtained from the Benesi–Hildebrand, Scott and Foster–Hammick–Wardley equations. The results indicate the formation of 1 : 1 charge transfer complex. The absorption band energy of the complex, E_{CT}, the ionization potential of the BPIE Schiff base ligand, I^{D}, and the Gibbs energy changes of the above reaction, ΔG^0, were calculated. Finally, the kinetics of the complex formation reaction were studied and was found to be second-order in each reactant. The values of the rate constants of the forward and reverse reactions k_1 and k_{-1} were determined.

Keywords: Di-Schiff base ligand; N,N′-bis(2-Pyridylmethylidene)-1,2-diiminoethane; Iron(III); Charge transfer complex; Spectrophotometry; Benesi–Hildebrand; Scott and Foster–Hammick–Wardley equations

1. Introduction

The reactions between electron donor and electron acceptor organic compounds which lead to the formation of charge transfer (CT) molecular complexes have been investigated by many researchers [1–11]. Some of these formation reactions complexes were finding a variety of applications in redox processes [12], pharmaceutical analysis [13–18], and surface chemistry [19]. They were also showing interesting physical properties such as electrical conductivity [2,20].

Compared with research work devoted to (CT) organic complexes studies involving benzoquinone derivatives π-acceptors [6,21–29] and iodine [1–3,8–10], little attention has been focused on the study of (CT) organometallic complexes of di-Schiff base ligands. Among the previous electronic spectrophotometric studies reported in the

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literature, the CT organic complexes using mono-Schiff base ligands as electron donors with various non metallic electron acceptors such as iodine and some π-acceptors [Chloranil (CA), 2,3-dichloro-5,6-dicyano-1,4-bezoquinone (DDQ), pentafluorobenzaldehyde (PFB)] are the most examined [30–36].

Several parameters concerning these ligands and their complexes such as the molar absorptivities, ε, the equilibrium constants, K, of their formation reactions, the absorption band energies of the complexes, E_{CT}, the ionization potentials of the ligands, I^{D}, and the Gibbs energy changes of the above reactions, ΔG^0 were established.

In this article, we investigated the spectrophotometric behavior of CT of another type of Schiff's base, viz., neutral di-Schiff base ligand, N,N′-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE), formed by the condensation of ethylenediamine with pyridine-2-aldehyde in 1 : 2 ratio. This type of ligand is known to form quadridentate complexes with a number of divalent cations [37–41] as well as to extract several metal ions in separation chemistry [42–44].

In addition to the establishment of the CT characteristics of the equilibrium between the BPIE ligand and iron(III) with their complex in methanol at 28°C, some complexation parameters such as K, ε, E_{CT}, I^{D} and ΔG^0 were determined. Moreover, the kinetics of the above complexation reaction were studied in methanol at 28°C by evaluating the order of the reaction and the rate constants of the forward and the reverse reactions k_1 and k_{-1}. As far as we know, no such study has been reported on this ligand with iron(III).

2. Experimental

2.1. *Materials*

Methanol and $FeCl_3 \cdot 6H_2O$ were obtained from Fluka. Pyridine-2-aldehyde and ethylenediamine obtained from Aldrich chemical, and were used without further purification.

The UV-visible spectra were measured using Perkin Elmer Lambda 20 and Shimadzu UV-1202 (Shimadzu Europa GMBH) UV-visible spectrometers with quartz cells of 1 cm path length. The infrared spectra of the donor were recorded using a Perkin-Elmer Paragon 1000 FT-IR spectrometer. The ^{1}H-NMR spectra were recorded in $CDCl_3$ by a Bruker AMX-300 Spectrometer. Chemical shifts are reported as δ values in ppm relative to an internal standard tetramethylsilane.

2.2. *Synthesis of the ligand*

The Schiff's base BPIE was prepared according to the literature as follows [45].

To an ethanolic solution of pyridine-2-aldehyde (0.08 mol) into a 250 cm^3 three-necked flask was added slowly (0.04 mol) of ethylenediamine in ethanol. After stirring the mixture for 2 h and the removal of the ethanol by rotary evaporation, an orange-yellow residual liquid product was obtained. The product was extracted with hot hexane several times. After cooling, an orange product was obtained and recrystallized from diethylether.

Yield, 52%. IR (KBr pellet, cm^{-1}): 1641(C=N). ^{1}H-NMR ($CDCl_3$, δ ppm): 4.05 (s, 4H, N–$(CH_2)_2$–), 8.40 (s, 2H, N=CH), 7.30 (m, 2H, Py), 7.71 (m, 2H, Py), 7.95 (m, 2H, Py), 8.62 (m, 2H, Py).

2.3. *Procedure of preparation of complex solutions*

The spectrometric spectra of the donor (BPIE), acceptor [iron(III)] and the complex were recorded in the region 200–800 nm.

The complex was prepared by mixing variable amounts of donor into a constant volume of the acceptor solution in methanol at 28°C. The donor concentration in the reaction mixture was varied over the range of 1×10^{-3} to 9×10^{-3} M, while the concentration of the acceptor was kept fixed at 1×10^{-3} M. The absorbencies of the mixtures at the wavelength of measurement (λ_{max}) which are due entirely to the complex, were measured using pure solvent, methanol, as the blank.

The kinetics measurements were performed in methanol at 28°C on equimolar sample of donor and acceptor (4.2×10^{-3} M). The measurements were followed kinetically at the complex wavelength (λ_{max}).

3. Results and discussion

3.1. *Identification of Fe(III)–BPIE complex*

The absorption bands for each of the electron donor (BPIE) and electron acceptor [iron(III)] solutions and their CT complex in methanol are tabulated in table 1.

Although neither individual solution of the iron(III) nor that of BPIE has absorption in the range of 400–800, the mixture had absorption maximum located at 583 nm, which is attributed to the formation of Fe(III)–BPIE complex. The appearance of this new absorption band is due to the complete electrons transfer from the donor to the unfilled orbital of the transition ferric ion.

3.2. *Determination of the complexation equilibrium constants*

The spectrophotometric data are employed to calculate the equilibrium constant, *K*, and the molar absorptivity of the complex, ε, for BPIE–Fe(III) complex in

Table 1. Wavelengths (nm) of the absorption bands of donor, acceptors, and complexes in methanol at 28°C.

	Acceptors		Complexes	
Donor (BPIE)	$FeCl_3 \cdot 6H_2O$	Iodine	BPIE–Iron(III)	BPIE–I_2
220	220	225	276	254
292	250	288	358	300
	365	360	583	386
		445		

methanol using the following Benesi–Hildebrand (1) [46], Scott (2) [47] and Foster–Hammick–Warley (3) [48] equations. These equations are based on the assumption of 1 : 1 (acceptor–donor) complex formation.

$$\frac{[\mathrm{A}]_0}{A} = \frac{1}{K\varepsilon[\mathrm{D}]_0} + \frac{1}{\varepsilon} \tag{1}$$

$$\frac{[\mathrm{D}]_0[\mathrm{A}]_0}{A} = \frac{[\mathrm{D}]_0}{\varepsilon} + \frac{1}{K\varepsilon} \tag{2}$$

$$\frac{A}{[\mathrm{D}]_0} = -K \cdot A + K \cdot \varepsilon \cdot [\mathrm{A}]_0 \tag{3}$$

where A denotes the optical density of the complex at $\lambda_{\max}$, $[\mathrm{A}]_0$ and $[\mathrm{D}]_0$ are the initial molar concentrations of acceptor and donor, respectively.

These equations are obviously of the type $y = ax + b$. After having determined the values of A experimentally, the corresponding y values were plotted against those of x term.

The plots reveal a good linearity between the two quantities in the three equations (figures 1–3) indicating the 1 : 1 stoichiometry of the CT complex. The values of a and b terms were calculated from the slopes and the intercepts of the straight lines. The values of K and ε are given in table 2. The values of K are: 46, 60, and 54 M^{-1}, while the values of ε are 254, 202, and 218 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ from equations (1), (2) and (3), respectively, which prove the validity of these equations for this reaction.

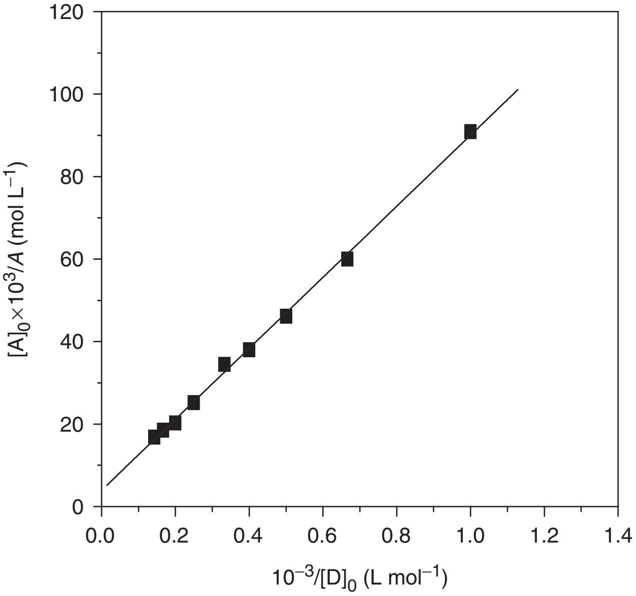

Figure 1. Plot of Benesi–Hildebrand's equation.

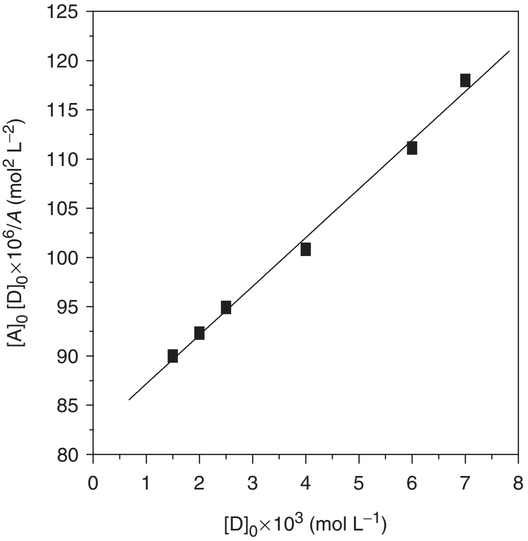

Figure 2. Plot of Scott's equation.

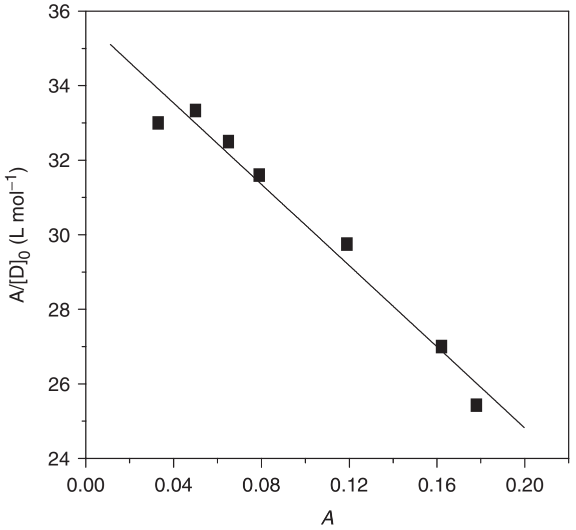

Figure 3. Plot of Foster–Hammick–Wardley's equation.

The CT complex can also be studied by evaluating it adsorption band energy, E_{CT} and the Gibbs energy changes, ΔG^0, calculated from λ_{max} and K values, respectively (table 2), applying the following equations:

$$E_{CT} = \frac{1243.667}{\lambda_{max}} \text{ (eV)} \tag{4}$$

$$\Delta G^0 = -RT \ln K. \tag{5}$$

Table 2. Equilibrium constants, molar absorptivities, absorption band energy, and Gibbs energy changes of complex formation reaction of BPIE–iron(III) in methanol at 28°C.

	Equation (1)	Equation (2)	Equation (3)
K (L mol^{-1})	46	60	54
ε (L cm^{-1} mol^{-1})	254	202	218
E_{CT} (eV)	2.133	2.133	2.133
$-\Delta G^0$ (kJ mol^{-1})	9.565	10.228	9.965

It is apparent that the formation of BPIE–Fe(III) complex takes place spontaneously and is energetically favored.

The ionization potential of the electron donor BPIE can be calculated from the (CT) absorption band for the iodine complex using the following equations [49–53]:

$$h \cdot \upsilon_{CT} = I^D - C_1 + \frac{C_2}{I^D - C_1} \tag{6}$$

$$h \cdot \upsilon_{CT} = aI^D + b \tag{7}$$

$$I^D = 4.39 + 0.857h\upsilon_{CT} \tag{8}$$

$$I^D = 5.1 + 0.7h\upsilon_{CT} \tag{9}$$

where a, b, C_1, and C_2 are constants of iodine, and their values are

$$a = 0.87, b = -3.6 \quad \text{or} \quad a = 0.67, b = -1.9, C_1 = 5.2\,\text{eV}, C_2 = 1.5\,\text{eV}^2.$$

and $h\upsilon_{CT}$ is absorption band energy of the CT complex.

In order to calculate the ionization potential of BPIE, we have studied the CT complex of this ligand with iodine in methanol at 28°C. Table 1 shows that the complex iodine–BPIE exhibit a new absorption band located at 386 nm. From this value, we established the ionization potentials of the Schiff base ligand according to equations (6)–(9) (table 3). The values of I^D range between 7.14 and 7.85 eV, while the average value obtained is 7.56 eV. This value is low compared with this of the unsubstituted pyridine rings (10.2 eV) [33]; this indicates that the donor group is the azomethine.

3.3. *Kinetic of CT-complex formation*

The kinetic of the reaction between the donor BPIE and the acceptor ferric ion was studied in methanol at 28°C and shown to be second-order using the following equations [54–57]:

$$\frac{x_e}{a^2 - x_e^2} \ln \frac{x_e(a^2 - xx_e)}{a^2(x_e - x)} = k_1 \cdot t = y \tag{10}$$

$$\frac{k_1}{k_{-1}} = \frac{x_e}{(a - x_e)^2} = K \tag{11}$$

Table 3. Calculated values of ionization potential of BPIE.

Equation	I^{D} (eV)
6	7.85
7	7.63
	7.83
8	7.14
9	7.35
Average value	7.56

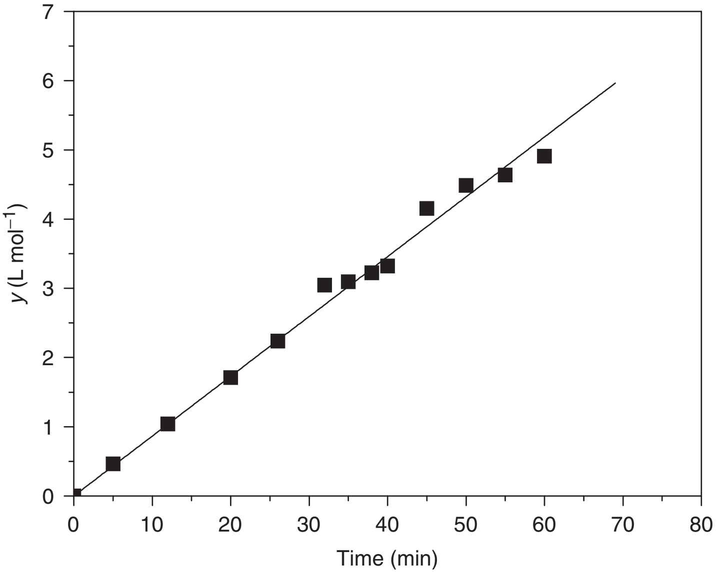

Figure 4. Plot of y *vs*. time.

where a is the initial concentration of donor and acceptor, x is the concentration of the complex, x_e is the concentration of the complex at equilibrium, and k_1 and k_{-1} are the rate constants of the forward and the reverse reaction.

The quantity y in equation (10) was plotted against time (figure 4), from which the rate constant k_1 of the forward reaction was calculated and the obtained value was $8.644 \times 10^{-2}\,\mathrm{M}^{-1}\,\mathrm{min}^{-1}$.

Using the value of the equilibrium constant, K, the value of the rate constant k_{-1} of the reverse reaction was calculated to be $1.88 \times 10^{-3}\,\mathrm{min}^{-1}$.

The vast difference between the value k_1 and k_{-1} indicate that the equilibrium is greatly oriented towards complex formation.

Finally, we have been carrying out more extensive studies on this type of polydentate di-Schiff base ligand with other transition metals, such as copper(II), cobalt(II), and nickel(II) and with non-metallic electron π-acceptors such as CA, DDQ, PFB.

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