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Spectrophotometric Studies of the Behavior of P-Amino-N, N-Dimethyl Aniline with Ferric Nitrate in Methanol

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The UV-visible absorption bands of the new complex were obtained using p-amino-N, N-dimethyl aniline as an electron donor with ferric nitrate as an electron acceptor in methanol at 25°C. The values of association constant K^{AD}, molar extinction coefficient ε^{AD}, and absorption band energy of charge transfer complex h ε_{CT} were calculated. The ionization potential of the donor I^{D}, was calculated from the complex band energy. The kinetics of the above association reaction were studied. This reaction was found to be a first order. The values of the rate constant of the forward reaction k$_1$, the rate constant of the reverse reaction k$_{-1}$, and the half-life t$_{1/2}$ were calculated.

Key Words: UV-visible spectrophotometry, charge transfer complex, Benesi-Hildebrand, Scott, Foster-Hammick-Wardley, association constant, molar extinction coefficient, ferric nitrate, methanol.

Introduction

Previous electronic spectrophotometric studies have been reported in the literature on complexes obtained by using electron donors with various electron acceptors in polar and non-polar solvents$^{(1-6)}$. These complexes were investigated and many different quantities and parameters concerning their behavior in those solvents, were calculated$^{(6-8)}$.

The association constant (K^{AD}) and molar extinction coefficients (ε^{AD}) were calculated using the following Benesi-Hildebrand$^{(9)}$, Scott$^{(10)}$ and Foster-Hammick-Wardley$^{(11)}$ equations respectively:

$$\frac{[A_o]}{A} = \frac{1}{K^{AD}\varepsilon^{AD}[D_0]} + \frac{1}{\varepsilon^{AD}} \tag{1}$$

where A = absorbance of the charge transfer band complex,

[A$_o$] = initial concentration of the electron acceptor,

[D$_o$] = initial concentration of the electron donor,

K^{AD} = association constant of charge transfer complex in solution, and

ε^{AD} = molar extinction coefficient of charge transfer complex.

$$\frac{[D_o][A_o]}{A} = \frac{[D_o]}{\varepsilon^{AD}} + \frac{1}{\varepsilon^{AD}K^{AD}} \tag{2}$$

$$\frac{A}{[D_o]} = -K^{AD}.A + K^{AD}\varepsilon^{AD}[A_o] \tag{3}$$

The charge transfer complexes can also be studied by evaluating their electronic absorption band energies. The ionization potentials of electron donors can be obtained from charge transfer absorption bands by using different approaches as in the following equations$^{(12-15)}$:

$$h\upsilon_{CT} = I^D - C_1 + \frac{C_2}{I^D - C_1} \tag{4}$$

$$h\upsilon_{CT} = aI^D + b \tag{5}$$

$$I^D = 4.39 + 0.857h\upsilon_{CT} \tag{6}$$

$$I^D = 5.1 + 0.7h\upsilon_{CT} \tag{7}$$

where h υ_{CT} = absorption band energy of charge transfer complex, and
I^D = ionization potential of the electron donor.
C_1 = 5.2 eV,
C_2 = 1.5 eV^2,
a = 0.67 or 0.87,
b = −1.9 or −3.6.

The kinetics of the association of electron donors with electron acceptors have been reported in the literature$^{(16-17)}$.

In this work, we investigated the kinetics of the equilibrium between p-amino-N, N-dimethyl aniline and ferric nitrate with their complex in methanol at 25°C, by calculating the equilibrium constant, and the order of the reaction as well as the rate constants of the forward and the reverse reactions. Moreover, the half-life period of the reaction was also obtained. In addition we calculated the ionization potential of the electron donor spectroscopically. The reason for choosing the above complexing agents is that its reaction was very slow and easy to measure. The importance of all calculations in this work is to prove the validity of equations (1-3) for this reaction. The effect of other solvents on the complex reaction will be sent for publication.

Experimental

p-Amino-N,N-dimethyl aniline (B.D.H) with a purity of 99.8%, ferric nitrate and methanol (Fluka) were used without further purification . The UV-visible spectra were measured using aPye Unicam SP8-100 spectrophotometer and a quartz cell of 1.0 cm path length. The complex was prepared by mixing variable amounts of donor solution into a constant volume of the acceptor solution in methanol. The donor concentrations ranged between 1x10^{-4} and 9x10^{-4} mol.dm^{-3} while the acceptor concentration remained constant (1x10^{-4}mol/dm^3).

Results and discussion

The absorption bands for each of the electron donor, electron acceptor and their charge transfer complex are tabulated in Table 1. The new absorption bands of the complex are 516 and 555 nm. The missing bands of donor are 418, 455, 538 and 205 nm, while the 360 nm band of the acceptor disappeared. The new absorption bands of the complex are located in the visible region probably due to the complete transfer of electrons from the donor, which has ionic properties, to the unfilled orbital of the transition ferric ion.

Table 1. Wavelengths (nm) of the absorption bands of the donor, acceptor and complex in methanol at 25°C.

Donor (p-A-DMA)	Acceptor Fe $(NO_3)_3 \cdot 9H_2O$	Complex
205	212	212
252	245	253
315	360	322
418		516
455		555
538		

Table 2 shows the values of molar extinction coefficients (ε^{AD}) of the complex in methanol at different donor concentrations at 25°C. These values range between 5100 and 2137 dm^3.cm^{-1}.mole^{-1}while the ratio $[D_o]/[A_o]$ = 1:1 to 9:1 respectively. This shows that lower amounts of donor are more sensitive to the absorption than higher concentrations. When equations (1), (2) and (3) were used and plotted, the values of K^{AD} and ε^{AD} for the complex were obtained as shown in Figures 1-3 and Table 3. The values of ε^{AD} are 2.9411 x 10^4, 2.148 x 10^4 and 3.80 x 10^4 while the values of K^{AD} are 1930, 2789 and 1071 dm^3.mole^{-1} from equations (1), (2) and (3) respectively.

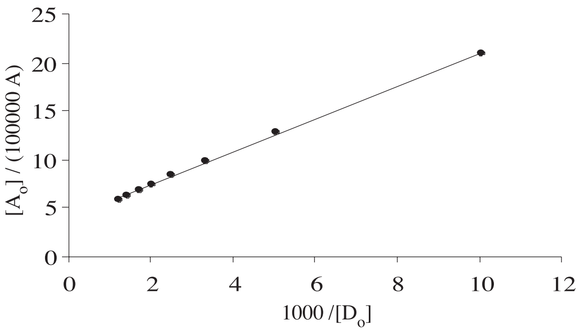

Figure 1. Plot of Benesi-Hildebrand's equation

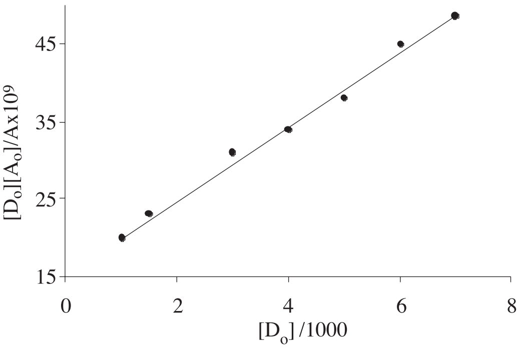

Figure 2. Plot of Scott's equation

These high values of K^{AD} may show the high stability of the complex in methanol solutions. Table 3 also shows the values of wave number in cm $^{-1}$ and energy in eV for the absorption band of the complex. At 555 nm the value of the wave number is equal to 18018 cm $^{-1}$ while its energy is equal to 2.235, which shows the high stability of the complex in methanol solution.

Table 4 shows the values of ionization potential of the donor calculated by using equations (4), (6) and (7). These values range between 6.305 and 6.820 eV, while the average value obtained is 6.600 eV.

Table 2. Molar extinction coefficients of the complex at different concentrations of the donor in methanol at 25°C.

$[D_o] \times 10^{-4}$ (mole . dm^{-3})	$[A_o] \times 10^{-4}$ (mole . dm^{-3})	ε^{AD} (dm^3 . cm^{-1} . $mole^{-1}$)
1	1	5100
2	1	3100
3	1	3110
4	1	2875
5	1	2602
6	1	2238
7	1	2366
8	1	2303
9	1	2137

Table 3. Values of association constants, molar extinction coefficient, wavelength, and energy of the absorption band of the complex in methanol at 25°C.

	Equation 1	Equation 2	Equation 3
K^{AD} (dm^3 . $mole^{-1}$)	1930	2789	1071
ε^{AD} (dm^3 . cm^{-1} . $mole^{-1}$)	29411	21480	38000
$\lambda_{\max}^{AD}$ (nm)	555	555	555
E_{CT} eV	2.235	2.235	2.235
Wave number (cm^{-1})	18018	18018	18018

Table 4. Calculated values of ionization potential of p-amino-N, N-dimethyl aniline.

Equation	I^D (eV)
4	6.820
6	6.305
7	6.665
Average value	6.600

The reaction of p-amino-N, N-dimethyl aniline as an electron donor with ferric ion as an acceptor is shown to be a first order reaction as in Figure 4. The rate constant (K_1) of the forward reaction was calculated from the graph and the obtained value was (0.02417) h^{-1}, from which the half-life ($t_{1/2}$) of 28.69 hours was obtained. When equilibrium is reached the above reaction may be written as follows:

$$D + A \rightleftharpoons C$$

where D, A and C represent the donor, acceptor and the complex respectively.

Using the values of the equilibrium constant shown in Table 3, the rate constant of the reverse reaction (k_{-1}) was calculated to be (9. 074x10 $^{-6}$) mole.dm^{-3}.h^{-1}. These values of K^{AD}, k_1 and k_{-1} show that the stability of the complex is very high and the forward reaction rate is much higher than the reverse reaction rate.

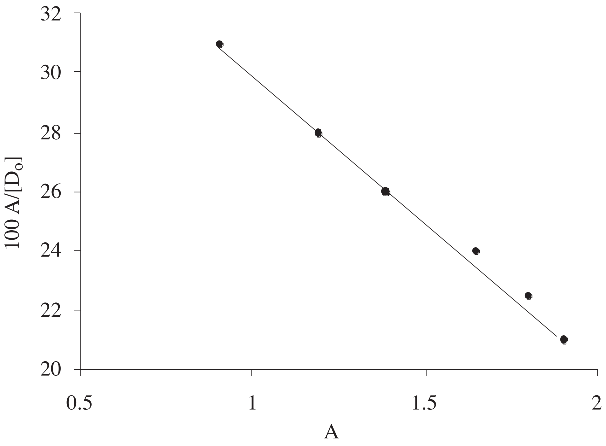

Figure 3. Plot of ammick-Wardley's equation

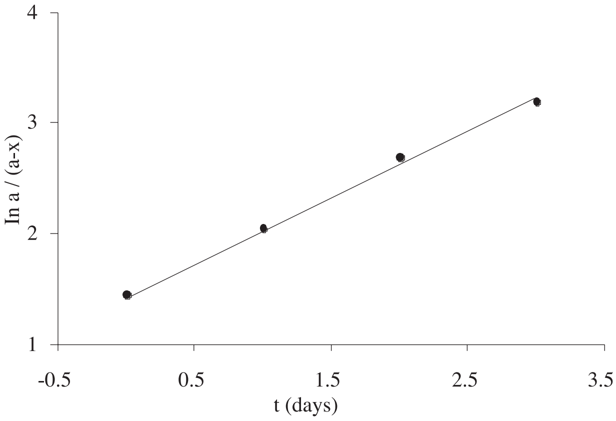

Figure 4. Plot of first order reaction equation

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