Solution and solid-state investigations of charge transfer complexes caused by the interaction of bathophenanthroline with different organic acceptors in a (methanol + dichloromethane) binary solvent system

Abdel Majid A. Adam [a,*], Moamen S. Refat [a,b]

[a] Department of Chemistry, Faculty of Science, Taif University, Al-Haweiah, P.O. Box 888, 21974 Taif, Saudi Arabia
[b] Department of Chemistry, Faculty of Science, Port Said University, Port Said, Egypt

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ABSTRACT

The present study investigated and compared the spectroscopic and structural morphology properties of bathophenanthroline (Bath) complexed with three organic acceptors (PA, DNBA and CLA) using a binary mixed solvent in both solution and solid-state. The products were fully characterized by physicochemical and spectroscopic techniques, such as UV–visible, IR, ^{1}H NMR, and ^{13}C NMR spectroscopies; XRD; SEM; TEM; and CHN elemental analysis. This work highlights that the binary solvent made of MeOH/CH$_2$Cl$_2$ at the molar ratio of 1:1 is an efficient media to form CT products with a highly organized and uniform morphology.

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1. Introduction

The charge transfer (CT) or proton transfer (PT) complex are formed from a weak interaction between an electron donor that has a sufficiently low ionization potential and an acceptor that has a sufficiently high electron affinity [1]. The formation of such complex is often characterized by the appearance of an intense, broad electronic absorption band in the UV–visible region that can be used for identification of the complex [2]. But, such band does not exist in the absorption spectra of both the donor and the acceptor species. The CT or PT interactions have attracted considerable interest due to their significant physical and chemical properties [3–11]. These interactions is of great importance in chemical and photochemical reactions, including addition, substitution, condensation [12], molecular self-assemblies [13,14], biochemical and bioelectrochemical energy-transfer processes [15], biological systems [16], and drug-receptor binding mechanisms [17–26]. Because of the high electrical conductivities of some CT or PT solid products, this complexation found many significant applications in electronics, optical devices, non-linear optical materials, electrically conductive materials, microemulsions, surface chemistry, photocatalysts, dendrimers, solar energy storage, organic semiconductors, and the investigation of redox processes [27–34]. The effects of solvent on the spectroscopic and thermodynamic properties of the CT or PT complexes have been extensively studied [35–45]. However, no studies have appeared in the literature on the effects on the structural morphologies of these complexes. For several years, we

have investigated the synthesis, characterization, and application of various CT and PT interactions [46–75]. As part of our continuing interest in this field, and because binary mixed solvents have been found to be more effective than single solvent systems in the preparation of particles with specific structures and particle size distributions [76], in this work we sought to obtain CT complexes of bathophenanthroline (Bath) with various organic acceptors (PA, DNBA, or CLA) in a methanol/dichloromethane solvent system, and to explore the benefits of using such binary mixed solvent in obtaining well-organized and uniformed CT products. The study focused on the following objectives:

- Synthesizing CT products of Bath with different organic acceptors (i.e., PA, DNBA, and CLA) in a 1:1 MeOH/CH$_2$Cl$_2$ solvent system;
- Characterizing the products stoichiometrically and spectroscopically based on spectral (UV–vis, IR, ^{1}H NMR, and ^{13}C NMR) and elemental data;
- Calculating and differentiating the spectroscopic data using the Benesi-Hildebrand equations;
- Obtaining the optical band gap from the absorption spectra to clarify the conductivity nature of the products;
- Observing and differentiating the products microstructures using XRD, SEM, and TEM techniques.

2. Experiments

2.1. Chemicals and solutions

All of the chemicals used were of analytical grade and were used as purchased. Bath (C$_{24}$H$_{16}$N$_2$; 332.4) was supplied by Sigma-Aldrich

Chemical Co. (USA) with a stated purity greater than 97% and was used without further purification. The organic acceptors picric acid (PA; $C_6H_3N_3O_7$; 229.10), 3,5-dinitrobenzoic acid (DNBA; $C_7H_4O_6N_2$; 212.12), and chloranilic acid (CLA; $C_6H_2Cl_2O_4$; 208.98) were purchased from Merck (Darmstadt, Germany) and were used without modification. HPLC-grade methanol and chloromethane were also purchased from Merck (Darmstadt, Germany). Standard stock solutions of the Bath and acceptors at a concentration of 5.0×10^{-3} M were freshly prepared prior to each series of measurements by dissolving precisely weighed quantities in a 100 mL volumetric flask. The stock solutions were protected from light. Solutions for spectroscopic measurements were prepared by mixing appropriate volumes of the Bath and acceptor stock solutions with the solvent immediately prior to recording the spectra.

2.2. Characterization techniques

The UV–Vis spectra were recorded in a solvent system over a wavelength range of 200–800 nm using a Perkin-Elmer Lambda 25 UV/Vis double-beam spectrophotometer with 1.0 cm quartz cells. The infrared (IR) spectra of the solid products (as KBr discs) were acquired at room temperature using a Shimadzu FT-IR spectrophotometer over the range of 4000–400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were collected on a Bruker DRX-250 spectrometer operating at 600 MHz. The measurements were performed at ambient temperature using DMSO-d_6 (dimethylsulfoxide, d_6) as the solvent and TMS (tetramethylsilane) as the internal reference. The X-ray diffraction (XRD) profiles were obtained using a PANalytical X'Pert PRO X-ray powder diffractometer. The instrument was equipped with a Ge(III) secondary monochromator, and Cu Kα_1 was employed as the radiation source with a wavelength of 0.154056 nm. The samples were scanned with 2θ between 5° and 90°. Scanning electron microscopy (SEM) images were obtained with Quanta FEG 250 emission scanning electron microscope operated at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1200 EX II transmission electron microscope operated accelerating voltage of 60–70 kV.

2.3. Stoichiometry determination

2.3.1. In solution-state

The stoichiometries of the CT interactions in solution-state were obtained from the spectrophotometric titrations by the determination of the conventional molar ratio according to previously published protocols [77]. These titrations were performed for the reactions of the Bath donor with each acceptor for their detectable CT bands. 0.25, 0.50, 0.75, 1.00, 1.50, 2.0, 2.50, 3.00, 3.50, or 4.00 mL of a standard solution (5.0×10^{-4} M) of the appropriate acceptor in the 1:1 MeOH/CH$_2$Cl$_2$ mixture was added to 1.00 mL of the Bath donor at 5.0×10^{-4} M dissolved in the same solvent mixture. The final volume of the mixture was 5 mL. The concentration of the donor (C_d) was maintained at 5.0×10^{-4} M, whereas the concentration of the acceptor (C_a) varied from 0.25×10^{-4} M to 4.00×10^{-4} M to produce solutions with a (donor:acceptor) molar ratio that varied from 4:1 to 1:4. The absorbance of each complex was plotted against the volume of the added acceptor.

2.3.2. In solid-state

The stoichiometries of the CT interactions in solid-state were obtained from elemental analyses of the carbon, hydrogen, and nitrogen contents determined with a Perkin-Elmer 2400 series CHN microanalyzer.

2.4. Preparation of the CT products

A simple synthetic protocol that was used for the preparation of CT complexes of Bath donor is briefly described as follows. First, 2 mmol of Bath donor in a 1:1 MeOH/CH$_2$Cl$_2$ mixture (20 mL) was added to 20 mL of a solution containing 2 mmol of the acceptor (either PA, DNBA or CLA) in the same solvent mixture. The resulting mixture was stirred at room temperature for approximately 0.5 h, where the resulting precipitation were isolated as shiny yellow, pale yellow, and violet crystals for Bath-PA, Bath-DNBA, and Bath-CLA products, respectively. The formed products were isolated, filtered, and further purified using solvent mixture and a recrystallization process to obtain the pure products. The products were then collected and dried in vacuo for 48 h. The products were characterized by spectroscopy (UV–Vis, IR, ^{1}H NMR, and ^{13}C NMR) as well as elemental analysis. The excellent agreement between the experimental and calculated values of C, H, and N indicates that the obtained products were free of impurities. The stoichiometry of the Bath interaction with the acceptors was found to have a 1:1 ratio.

Elemental analysis, as percentages, was determined for the Bath-PA product ($C_{30}H_{19}N_5O_7$; 561.5). Calculated values were C, 64.17%; H, 3.41%; N, 12.47%. Experimentally determined values were C, 64.09%; H, 3.38%; N, 12.41%.

For the Bath-DNBA product ($C_{31}H_{20}N_4O_6$; 544.51), calculated values were C, 68.38%; H, 3.70%; N, 10.29%. Experimentally determined values were C, 68.34%; H, 3.76%; N, 10.33%.

For the Bath-CLA product ($C_{30}H_{18}Cl_2N_2O_4$; 541.38), calculated values were C, 66.56%; H, 3.35%; N, 5.17%. Experimentally determined values were C, 66.51%; H, 3.29%; N, 5.13%.

3. Results and discussion

3.1. Solution-state properties

3.1.1. UV–visible measurements

The Bath donor (5.0×10^{-4} M) was mixed with each acceptor solution (5.0×10^{-4} M) in the solvent system, and the reaction was allowed to proceed at room temperature. The electronic absorption spectrum of each reaction mixture was then recorded against a reagent blank solution. A change in the color of the solutions was observed as the Bath and acceptor solutions were mixed. These changes provide strong evidence of CT interactions between the Bath and the acceptors. Fig. 1 displays the UV–visible absorption spectra in the region of 200–800 nm of the Bath donor and acceptors along with those of the synthesized complexes. It is obvious from the spectra that each complex exhibits a maximum absorption peak (λ_{max}) in the UV–visible range with different intensities for Bath-PA (285 and 355 nm), Bath-DNBA (270 nm), and Bath-CLA (275 nm). These strong absorption bands are presumably caused by the donor-acceptor interactions and are indicative of the formation of a CT complex. The Bath donor displays a strong broad band at 280 nm, while acceptors display small absorption band at that wavelength. On mixing the solutions of the donor and acceptor, this characteristic band shifts, increases greatly in intensity, becomes more broad, and is centered at 285, 270, and 275 nm for the Bath–PA, Bath–DNBA, and Bath–CLA complexes, respectively.

3.1.2. Stoichiometry in solution

The stoichiometry of the Bath-acceptor interaction in solution was obtained by applying a varying molar ratio spectrophotometric titration method. The electronic spectra of the interactions were recorded at varying acceptor concentrations and a constant Bath donor concentration. The composition of the complex was determined graphically by plotting the absorbance on the ordinate against the volume of the acceptor (in mL) on the abscissa. Representative spectrophotometric titration plots based on the characterized absorption bands are shown in Fig. 2. The results show that the greatest interaction between Bath donor and acceptors occurred at a donor: acceptor ratio of 1:1, indicating that 1:1 CT complexes were formed. These stoichiometric values are consistent with the data obtained by the elemental analysis of the solid-state complexes.