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Determination of the formation constant for the inclusion complex between Lanthanide ions and Dansyl chloride derivative by fluorescence spectroscopy: Theoretical and experimental investigation

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ABSTRACT

In this paper, a sensitive, easy, efficient, and suitable method for the calculation of K_f values of complexation between one derivative of Dansyl chloride [5-(dimethylamino) naphthalene-1-sulfonyl 4-phenylsemicarbazide] (DMNP) and Lanthanide(III) (Ln) ions is proposed, using both spectrofluorometric and spectrophotometric methods. Determination of K_f showed that DMNP was mostly selective towards the erbium (III) ion. The validity of the method was also confirmed calculating the Stern–Volmer fluorescence quenching constants (K_{sv}) that resulted in the same consequence, obtained by calculating the K_f of complexation values. In addition, the UV–vis spectroscopy was applied for the determination of K_f only for the Ln ions that had interactions with DMNP. Finally, the DFT studies were done on Er^{3+} and the DMNP complex for distinguishing the active sites and estimating the pair wise interaction energy. It can be concluded that this derivative of Dansyl chloride with inherent high fluorescence intensity is a suitable reagent for the selective determination of the Er^{3+} ion which can be used in constructing selective Er^{3+} sensors.

1. Introduction

Recently, the properties of Lanthanide organic complexes have been extensively studied [1–3]. These complexes play an important role in different areas of chemistry, e.g. as catalysts in organic syntheses, as shift reagents in nuclear magnetic resonance spectroscopy and for light converters [4]. Luminescent Lanthanide complexes [5–7] have attracted vast areas of research from both material and biological sciences [8,9] mainly due to their very narrow emission bands and Large Stokes shifts, etc [10]. The probes based on erbium ion are of special interest because erbium organic complexes have attracted much attention for their potential applications in polymeric and organic–inorganic derived systems [11].

The absorption and emission of Ln ions originates from f–f transitions which are forbidden by spectral selection rules. In practice this means that both absorption and emission are very weak. Therefore, using appropriate ligands can lead to enhancement of the f–f electronic transitions through an intersystem energy transfer process [12–14]. The ligand is able to enhance the Ln fluorescence intensity for three reasons: (1) it increases the quantum yield of emission, (2) it can absorb light efficiently and transfer absorbed energy onto the complexed Ln ion and (3) the ligand provides a means to add a reactive functional group to link the Ln complex to a target molecule. Complexes of Ln ions with organic ligands have also been doped in polymers for optical amplification [15,16].

The biological properties of the Ln ions, primarily based on their similarity to calcium, have been the basis for research into potential therapeutic applications of Lns since the early part of the twentieth century [17–19].

In the last few years, many various derivatives of Dansyl chloride (5-dimethylamino-1-naphthalenesulfonyl chloride) as a complexing agent have been extensively used in different studies [20–24]. Dansyl and its derivatives can be applied as synthetic receptors to selectively bind a wide variety of guest molecules/ions forming the host–guest complexes [25,26].

Dansyl chloride is a yellow crystalline powder that reacts violently with water. Materials hydrolyze in contact with moisture/water releasing toxic and corrosive fumes of hydrogen chloride and aqueous hydrochloric acid. Hydrochloric acid solutions react with most metals forming flammable hydrogen gas. This complex-

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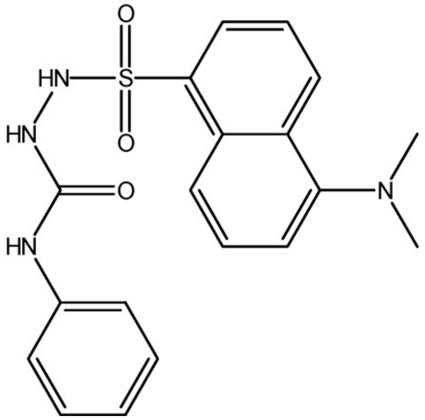

Fig. 1. Structure of 5-(dimethylamino) naphthalene-1-sulfonyl-4-phenylsemicarbazide.

ing agent is incompatible with amines, strong oxidizing agents, and strong bases. As its hazardous decomposition products we can refer to hydrogen chloride, nitrogen oxides, carbon monoxide, oxides of sulfur, carbon dioxide and chlorine. Dansyl chloride can also be dangerous to respiratory system, eyes, skin, and mucous membranes. Dansyl chloride derivatives are fluorometric detection reagents emitted by UV light, and can be extensively used as a fluorescent label in immunofluorescence methods as well as in yielding fluorescent N-terminal amino acids and peptide derivatives. So, in order to decrease the risk of generating contaminant and hazardous agents, we used a non-polluting derivative of Dansyl (DMNP) (Fig. 1) that had a good fluorescence property, to investigate the interactions between this ligand and all Ln ions. This was done by studying the fluorescence quenchings and UV–vis red shifts caused by titring the ligand with the Ln ions.

For the purpose of verifying these complexations, it is essential that we find each ligand–Ln's formation constant in the acetonitrile media and compare them with one another to see with which Ln ion, DMNP interacts most selectively.

Although DMNP was demonstrated to have interactions with five Lanthanide ions [Ln = La (III), Gd (III), Tb (III), Dy (III) and Er (III)], gathering information released by calculating each Ln–ligand formation constant, showed that this complexing agent interacts selectively with Er (III) ion. This result was confirmed assembling the UV–vis spectra of titring DMNP with each of the five mentioned Ln ions, and also by calculating the fluorescence quenching constants ($K_{\text{Stern–Volmer}}$) values.

In order to calculate the formation constants of the complexation, the fluorescence spectra of the titration of DMNP with all Ln ions, and also the UV–vis spectra of the titration of this ligand with the five Ln ions DMNP interacted with, were applied.

In recent years, the DFT method was applied in different branches of chemistry [27–36].

In the present paper, we used the recently introduced approximate DFT method, DFTB (density functional tight-binding), extended by the empirical London dispersion energy term, which is accurate and reliable for computational studies [37].

2. Experimental

2.1. Reagents

All the chemicals used were of analytical reagent grade and were used without further purification. Acetonitrile and nitric acid were obtained from Merck.

Ln (III) nitrates were prepared by dissolving Ln oxides in a nitric acid aqueous solution. The procedure for synthesizing of 5-(dimethylamino) naphthalene-1-sulfonyl-4-phenylsemicarbazide is as follows: the N-phenylhydrazinecarboxamide (2 mmol, 0.302 g) was solved in acetone and three drops of triethylamine was added. After that 5-(dimethylamino) naphthalene-1-sulfonyl chloride (2 mmol, 0.468 g) was added to the solution of N-phenylhydrazinecarboxamide at room temperature. Then, the solid product was crystallized in ethanol.

In order to confirm the (DMNP) structure, the relative NMR spectrum is attached. ^{1}H NMR (90 MHz, $CDCl_3$): σ_H 3.02 (6H, S, NMe_2), 7.00 (1H, t, J = 7.5 Hz, CH), 7.23 (2H, dd, J = 7.5, 7.8 Hz, 2CH), 7.35 (2H, d, J = 7.6 Hz, 2CH), 7.40 (1H, d, J = 6.4 Hz, CH), 7.56 (1H, dd, J = 6.4, 8.4 Hz, CH), 7.80 (1H, dd, J = 6.6, 8.5 Hz, CH), 8.12 (1H, d, J = 8.5 Hz, CH), 8.22 (1H, d, J = 6.6 Hz, CH), 8.33–8.40 (3H, br, 3NH). ^{13}C NMR (400 MHz, $CDCl_3$): σ_C 39.84 (NMe_2), 116.21, 118.33, 123.60, 124.72 (4CH), 125.91 (C), 126.05, 127.77, 128.70, 131.63, 133.14 (5CH), 134.41, 139.95, 154.39 (3C), 152.55 (C=O).

2.2. Sample treatment

For the fluorescence and UV–vis studies, solutions of DMNP were: 5×10^{-6} mol L^{-1} and 5×10^{-5} mol L^{-1} respectively. The Ln ions standard solutions (1.0×10^{-4} mol L^{-1}) and (1.0×10^{-3} mol L^{-1}) were also prepared for fluorescence and UV–vis verifications in acetonitrile, respectively.

2.3. Apparatus and software

The fluorescence study was performed using a Perkin-Elmer LS50 spectrofluorimeter. The software used to record fluorescence spectrum was FL-winlab. Experiments were carried out at ambient temperature (25 °C) with magnetic stirring in the fluorimeter cell. The excitation wavelength was 325 nm in all cases with an excitation and emission band pass (slit) of 8 nm and scan rate of 1500 nm/min. The solutions were placed in a 1 cm path-length quartz cell for the fluorescence measurements. No explicit correction of our spectra for the instrument response was performed because in our experiments only relative changes in the fluorescence intensity of the Ln ions as a function of certain experimental conditions were required.

The UV–vis study was carried out with a Perkin Elmer Lambda 800 spectrophotometer (slit width of 1 nm and scan rate of 400 nm/min) using 1.00 cm quartz cell. Spectra were acquired over the wavelength range of 200–800 nm against a blank (the acetonitrile solution).

All the spectra are given to DATAN 3.1, which is a program used in this study to determine the K_f of complexation.

3. Results and discussions

3.1. Intrinsic Dansyl fluorescence

As Dansyl derivatives have widespread applications as fluorescent ligands, in this research it was decided to investigate the interaction of DMNP with all Ln ions, and also to determine the formation constant of the complex (K_f) being formed using fluorescence spectroscopy.

The type of interaction between DMNP and Lanthanide ions is charge–dipole. Due to the existence of three oxygen and three nitrogen atoms in the structure of DMNP as donor atoms (hard and intermediate properties) and relatively intermediate properties of Lanthanide ions, there exists a charge–dipole interaction. Due to the semi-cavity of DMNP and size of Lanthanide ions, a range of formation constant will be obtained.

The intrinsic fluorescence of DMNP was obtained at 435 nm when excited at 325 nm. A quantitative analysis of the potential