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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 $K_{\rm f}$ values of complexation between one derivative of Dansyl chloride [5-(dimethylamino) naphthalene-1-sulfonyl 4phenylsemicarbazidel (DMNP) and Lanthanide(III) (Ln) ions is proposed, using both spectrofluorometric and spectrophotometric methods. Determination of $K_{\rm f}$ 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 $K_{\rm f}$ of complexation values. In addition, the UV-vis spectroscopy was applied for the determination of $K_{\rm f}$ 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 Er³⁺ ion which can be used in constructing selective Er³⁺ sensors.

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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

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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 Nphenylhydrazinecarboxamide at room temperature. Then, the solid product was crystallized in ethanol.

In order to confirm the (DMNP) structure, the relative NMR spectrum is attached. ¹H NMR (90 MHz, CDCl₃): $\sigma_{\rm H}$ 3.02 (6H, S, NMe₂), 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). ¹³C NMR (400 MHz, CDCl₃): $\sigma_{\rm C}$ 39.84 (NMe₂), 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: $5 \times 10^{-6} \text{ mol } L^{-1}$ and $5 \times 10^{-5} \text{ mol } L^{-1}$ respectively. The Ln ions standard solutions $(1.0 \times 10^{-4} \text{ mol } L^{-1})$ and $(1.0 \times 10^{-3} \text{ mol } L^{-1})$ 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 ($25 \circ C$) 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 acetoni-trile solution).

All the spectra are given to DATAN 3.1, which is a program used in this study to determine the $K_{\rm f}$ 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

interaction between Ln ions and DMNP was performed on fluorometric titration. A 3 mL solution containing 5×10^{-6} mol L⁻¹ of DMNP was titrated by successive additions of Ln solutions of 1×10^{-4} mol L⁻¹ (to give a final concentration of 10^{-5} mol L⁻¹), and the fluorescence intensity was measured.

3.2. Lanthanides fluorescence

The Lanthanides are unique fluorescent metals. Their absorption coefficients are low, and their emission ratios are slow. As an outcome, they are not usually directly excited. In fact, they can be excited through chelated organic or bio-organic molecules [38,39]. The elements of the Ln series display different properties (size, charge densities, hydration energy) in comparison with the other elements of the periodic table. The effective ionic radii of the trivalent Ln cations typically decrease in the order of atomic numbers. However, no direct correlation between the ionic radii and the formation constant is observed.

Fig. 2a–e shows the spectra for the titration of DMNP by five Lanthanide ions ($Ln = Er^{3+}$, Dy^{3+} , Gd^{3+} , Tb^{3+} , La^{3+}), respectively.

The DMNP instinct fluorescence intensity is about 900 when excited at 325 nm, and the emission wavelength was observed at 435 nm. The fluorescence intensity was quenched by titrating DMNP with the five Ln ions. As can be seen in these plots, the high-



Fig. 2. The fluorescence spectra of the titration of 5×10^{-6} mol L⁻¹ of DMNP by 10^{-4} mol L⁻¹ solutions of Ln ions at 25 °C excited at 325 nm. (a) Er³, (b) Dy³⁺, (c) Gd³⁺, (d) Tb³⁺, (e) La³⁺.



Fig. 3. Maximum fluorescence intensity versus concentration of Er³⁺.



Fig. 4. $[Er^{3+}]/[L]$ mole ratio plot at $\lambda_{em} = 435$ nm, M/L = 1/1.

est amount of fluorescence quenching is concluded when titring DMNP with Er^{3^+} .

The fluorescence quenching refers to any process decreasing the fluorescence intensity of a given substance. There are mainly two types of quenching. The collisional quenching, which results from the collision between fluorophores and a quencher [40], and the static quenching, that is due to the formation of a ground-state complex between fluorophores and a quencher [41]. In this case, the formation of complex between the fluorophore (DMNP) and quenchers (Ln ions) suggests the existence of static quenching.

The maximum intensity of fluorescence in the quenching region of DMNP versus concentration of Er^{3+} is shown in Fig. 3. There is an exponential decrease in the fluorescence of DMNP with increasing concentration of the Lanthanides it had interacted with [Ln = La (III), Gd (III), Tb (III), Dy (III) and Er (III)] in the quenching region. As this figure shows, the intensity decreases as the concentration of Er^{3+} increases up to 0.1 μ mol L⁻¹.

In this study, the ligand to Ln mole ratio was calculated by fluorescence method. Fig. 4 displays a fluorescence intensity of $5\times 10^{-6}\,mol\,L^{-1}\,$ DMNP which has been titrated by erbium $(1\times 10^{-4}\,mol\,L^{-1})$ versus $Er^{3+}/DMNP$ mole ratio. The resulted data showed this ratio to be 1:1, which provide evidence that each DMNP molecule can be saturated with the studied Ln ions in the mole

ratio of 1 to 1. Therefore, the formation constant values ($K_{\rm f}$) of the resulting 1:1 complexes could be evaluated in all cases.

The reasons this technique was used are due to its; simplicity, ease of accessibility, high fluorescence property of DMNP, distinct observation of fluorescence quenching in the case of titring DMNP with the Ln ions it had interaction with, and presence of aromatic rings in the host molecule structure.

3.3. Calculations of K_f of complexation

3.3.1. Fluorescence spectra

Based on Fig. 2, DMNP, has interactions with five Lanthanide ions [Ln = La (III), Gd (III), Tb (III), Dy (III) and Er (III)]. In order to determine which Ln ion this ligand interacts the best with, we have to calculate the formation constant of the complexations. The obtained K_f values calculated by fluorescence spectra are listed in the first row of Table 1. The highest log K_f value was obtained for Er³⁺ (7.53) in contrast to that of Sm³⁺ which is the least (3.84) and observed order in this table acquired for other Ln ions.

3.3.2. UV-vis spectra

The complex formation is further evidenced by UV–vis spectra. The second row of Table 1 shows the obtained K_f values for the first five Ln ions complex with DMNP, calculated by UV–vis spectra. These Ln ions are the cations DMNP interacted with.

As seen, the values calculated with the UV–vis spectra for the Lns–DMNP complexation formation constant are in satisfactory agreement with those obtained with the fluorescence spectra. According to Fig. 2 and Table 1, DMNP has the most interaction and selectivity to Er^{3+} . This result is further approved by calculating the Stern–Volmer quenching constants.

3.4. The Stern–Volmer quenching constant

The quenching can be mathematically expressed by the Stern–Volmer Eq. (1), which allows for calculating quenching constants [42].

$$\frac{F_0}{F} = 1 + k_q \tau_0[Q] = 1 + K_{\rm sv}[Q] \tag{1}$$

where F_0 and F are the fluorescence intensities in the absence and presence of the quencher, k_q is the bimolecular quenching constant, τ_0 is the lifetime of the fluorescence in the absence of the quencher [Q] is the concentration of the quencher, and K_{sv} is the Stern–Volmer quenching constant. In the presence of a quencher (Lns), the fluorescence intensity is reduced from F_0 to F. The ratio (F_0/F) is directly proportional to the quencher concentration [Q].

Evidently:

$$K_{\rm sv} = k_{\rm q} \tau_0 \tag{2}$$

$$\frac{F_0}{F} = 1 + K_{\rm sv}[Q] \tag{3}$$

According to Eq. (3), a plot of F_0/F versus [Q] shows a linear graph with an intercept of 1 and a slope of K_{sv} [43]. A typical plot of F_0/F versus Er^{3+} concentration is shown in Fig. 5. The resulting regression equations for all Ln ions are summarized in Table 2.

As known, $K_{\rm f}$ is a parameter used in this work to evidence the quantity of interactions between DMNP and Ln ions, besides $K_{\rm sv}$ values show the amount of fluorescence quenching caused by the

The obtained K_f values calculated by fluorescence and UV-vis spectra.

Table 1

Lanthanide Ion (III)	Er	Dy	Gd	Tb	La	Nd	Ce	Pr	Но	Yb	Eu	Lu	Tm	Sm
Log K _f (FL)	7.53	6.02	5.79	5.47	5.37	4.33	4.27	4.21	4.15	4.03	4.01	3.98	3.92	3.84
$\log K_{\rm f} ({\rm UV})$	7.2	5.91	5.53	5.4	5.23	-	-	-	-	-	-	-	-	-



Fig. 5. The Stern–Volmer plot of the titrations of DMNP with different concentrations (μ mol $L^{-1})$ of $Er^{3+}.$

Table 2

The Stern-Volmer equations for different Lns.

Ln ions	Stern-Volmer equation	$F_0/F = 1 + K_{sv}[Q]; Y = F_0/F; X = [Q]$				
	R ²	Related equation				
Er ³⁺	0.9937	<i>y</i> = 5,000,000 <i>x</i> + 0.6405				
Dy ³⁺	0.9914	y = 3,000,000x + 0.7209				
Gd ³⁺	0.9929	y = 2,000,000x + 1.1915				
Tb ³⁺	0.9958	y = 1,600,000x + 1.1314				
La ³⁺	0.9903	y = 1,000,000x + 1.3678				
Nd ³⁺	0.9919	y = 73,881x + 1.0356				
Ce ³⁺	0.9934	y = 43,399x + 1.0144				
Pr ³⁺	0.9973	y = 40,886x + 1.0620				
Ho ³⁺	0.9935	y = 35,731x + 1.0768				
Yb ³⁺	0.9915	y = 29,676x + 1.0743				
Eu ³⁺	0.9943	y = 29,171x + 1.0534				
Lu ³⁺	0.9989	y = 20,738x + 0.9898				
Tm ³⁺	0.9956	y = 19,831x + 1.0485				
Sm ³⁺	0.9906	y = 8146.6x + 0.9968				



Fig. 6. Colleration plot of *K*_f versus *K*_{sv}.

formation of complex between DMNP and Ln ions. More quantity of interactions leads to more fluorescence quenching, so further obtained amount of K_f means further K_{sv} value. As it is apparent in Tables 1 and 2, the K_{sv} values consequence corresponds exactly to that of the K_f values of the Ln–DMNP complexation. Investigation of colleration between K_f and K_{sv} demonstrated that the results are reliable and Fig. 6 shows the K_f versus K_{sv} with $R^2 = 0.955$.

4. Computational studies

Many experimental and theoretical investigations have been carried out for further comprehension of the fundamental interaction between metal ions and neutral molecules, also their relationship to molecular recognition. Computational models capa-



Fig. 7. Plot of *K*_f values versus interaction energy by DFT method.

ble of reliably predicting ligand selectivity in a variety of cations have proven to be valuable tools for the advancement of practical works [28–32].

Quantum methods for binding of Lanthanide systems have grown recently [44–46]. But Lanthanum metals are heavy atoms and application of calculation method for these ions is expensive and time consuming, so these issues develop no more [46–48]. In this work we applied SBKJC/6-31G* that is high level of theory and results are very accurate, for investigation of binding energy with supercomputer. In addition, these calculation methods help us for tendency of different lanthanums ion to different ligands and understanding of interaction between them.

In order to have a clear picture about the selectivity of ligand for various metal ions, in this work, we investigated its binding to Ln ions by using the Gamess software with SBKJC/6-31G* calculations [49]. The binding energy (ΔE) was calculated using Eq. (4) [33,34]:

$$\Delta E = \Delta E_{\text{complex}} - (\Delta E_{\text{ligand}} - \Delta E_{\text{cation}}) \tag{4}$$

where $\Delta E_{\text{complex}}$, ΔE_{ligand} and ΔE_{cation} are the total energies of the complex, un-complexed ligand and metal ion, respectively. Fig. 7 shows the interaction energy versus K_{f} for different Ln ions. Inspection of Fig. 1 reveals that the cation binding energy with ligand shows a pronounced dependence on the nature of metal ions used.

Thus, based on the above calculation results, DMNP could possibly be used as a suitable ligand to interact with Er^{3+} . Fig. 8 shows the optimized structure of DMNP with the minimum level of energy. The heteroatoms in the DMNP structure which are closer to Er^{3+} ion are those that had most interaction with this ligand.



Fig. 8. Optimal conformation of the DMNP with Er (III) (without hydrogen atoms).

5. Conclusion

Lanthanide ions generally exist together in trace amounts, and separation of them with non-expensive methods has always been of high interest. In this study, we used one derivative of Dansyl (DMNP) that had high fluorescence and UV–vis properties, as a ligand, and titred it with all Ln ions to verify the ligand–Lns complexations. The results showed that the applied derivative of Dansyl has interaction with five Lanthanides [Ln = La (III), Gd (III), Tb (III), Dy (III) and Er (III)]. We calculated the formation constants of the complexations applying both spectrofluorometric and spectrophotometric methods, in order to realize which Ln ion DMNP interacts with most selectively. Conclusions showed that the applied Dansyl responses are mainly selective towards the Er^{3+} ion. The employed methodology was confirmed by calculating the Stern–Volmer quenching constant values, as the K_{sv} values sequence was in satisfactory agreement with the calculated K_f of complexation values.

These results can be employed in constructing specific sensors of Er (III) that can be helpful in separating the Ln ions existing in trace amounts in a medium together, which is of high value.

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