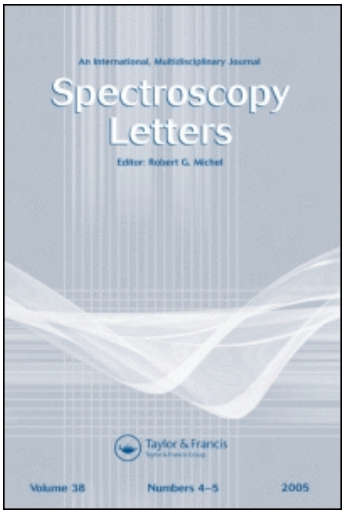

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

The Solvent Influence on the Fluorescence Behaviour of the Lithium-Tetracycline System

Eva M. Almansa López[a]; Luis Cuadros Rodriguez[a]; Ana García Campana[a]; Manuel Román Ceba[a]
[a] Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Granada, Spain

To cite this Article López, Eva M. Almansa , Rodriguez, Luis Cuadros , Campana, Ana García and Ceba, Manuel Román(1999) 'The Solvent Influence on the Fluorescence Behaviour of the Lithium-Tetracycline System', Spectroscopy Letters, 32: 1, 73 — 82
To link to this Article: DOI: 10.1080/00387019909349968
URL: http://dx.doi.org/10.1080/00387019909349968

SPECTROSCOPY LETTERS, 32(1), 73-82 (1999)

THE SOLVENT INFLUENCE ON THE FLUORESCENCE BEHAVIOUR OF THE LITHIUM–TETRACYCLINE SYSTEM

Key words: Tetracycline, Lithium, Fluorescence enhancement, Solvent influence

Eva M. Almansa López, Luis Cuadros Rodríguez*, Ana M. García Campaña and Manuel Román Ceba

Department of Analytical Chemistry, Faculty of Sciences, University of Granada c/ Fuentenueva s.n., E-18071 Granada, Spain

Abstract

The fluorescence of the lithium–tetracycline system is studied and discussed in terms of several water–miscible solvents. The excitation and emission spectra of the system are compared with both corresponding lithium and tetracycline blanks. Only two different spectra patterns are found to be the most fluorescence enhanced in the presence of non–hydroxylic solvents.

*Corresponding author (FAX 34 958 243326)

Introduction

The modification of tetracycline native fluorescence (shift of maximum wavelength spectrum or enhancement of the emitted intensity) by formation of quelates with di–or trivalent metallic cations (beryllium, magnesium, calcium and aluminium) in order to improve the performance characteristics of the fluorimetric and/or chromatographic (fluorescence detection) determination methods of these antibiotics, has been widely used in Analytical Chemistry since the 1960s[1]. More recently, with the same aim, some lanthanide ions, such as europium or terbium, have been used as acceptors in sensitised luminescence for the detection and determination of tetracyclines[2,3].

The lithium ion forms fluorescent species with some fluorogenic organic reagents, such as the α–hydroxyderivatives of anthraquinone, in alkaline medium and in the presence of certain cation–solvating solvents[4,5]. However, this system has recently been applied to lithium determination in some matrix samples such as spring waters, drugs or biological fluids, though no analytical applications on the determination of the organic substrate have been described.

Because of the similar quinoid structure of the tetracyclines to that of the α–hydroxyanthraquinones, the lithium ion presents a great potential as a fluorogenic reagent for the analysis of tetracycline (TC) and its derivatives. This paper describes the influence of the solvent on the fluorescent behaviour of the Li–TC species and it constitutes the first report in the scientific literature on the fluorescence of this system. Further investigations are being carried out by our research group to establish its analytical applications.

Experimental

Equipment

The fluorescence was monitored with a Perkin–Elmer MPF–66 spectrofluorimeter, with two matched 1 cm quartz cells, thermostatically controlled at 25.0 ± 0.5 ºC with a water–bath circulator (Frigiterm S–382, J. P. Selecta).

Table 1. Experimental values of maximum excitation and emission wavelength, fluorescence signals for TC-Li system and SEF^{TC} with 14 solvents. (Solution-type I). (Excitation and emission slits, 5 nm).

Solvent	λ_{exc}/nm maximum	λ_{em}/nm maximum	Spectral* pattern	TC–Li signal	SEF^{TC}**
Water	363	464	E	60.9	0.96
Methanol	377	537	E	203.4	1.30
Ethanol	379	510	E	149.8	2.96
1-Propanol	353	465	E	189.2	1.38
2-Propanol	282	538	E	218.4	2.87
Ethylenglycol	375	538	E	302.6	1.68
Glycerine	372	570	E	424.2	0.90
Acetone	403	501	E	179.3	3.90
DMF	408	468	D	420.5	5.50
DMS	407	467	D	426.7	3.25
HMPT	356	425	–	396.2	0.83
Acetonitrile	403	501	E	133.2	4.99
THF	377	538	E	490.7	1.48
1,4-Dioxan	384	480	E	220.4	3.89
Pyridine	407	472	D	373.3	3.72

* E: Spectral pattern similar to ethanol (Fig. 2) and D: Spectral pattern similar to DMS (Fig. 1)

** SEF^{TC}=TC fluorescence-signal enhancement factor, calculated as Li-TC signal/TC-blank signal.

Fluorescence data were obtained with spectral correction. A 101 Rhodamine quantum counter sample was used for source intensity adjustment and for generating correction factors. Perkin–Elmer attenuators CP 36167-0 (4% open), CP 36056-0 (9% open), CP 36057-0 (12% open), CP 36058-0 (20% open) and CP 36059-0 (30% open) were used to attenuate the fluorescence signals.

Chemicals

Tetracycline (TC) working solution was prepared from Tetracycline Hydrochloride (SIGMA) in water. Solutions of sodium hydroxide and lithium (I) were prepared by dissolving NaOH (MERCK) and $LiNO_3$ (MERCK) in water.

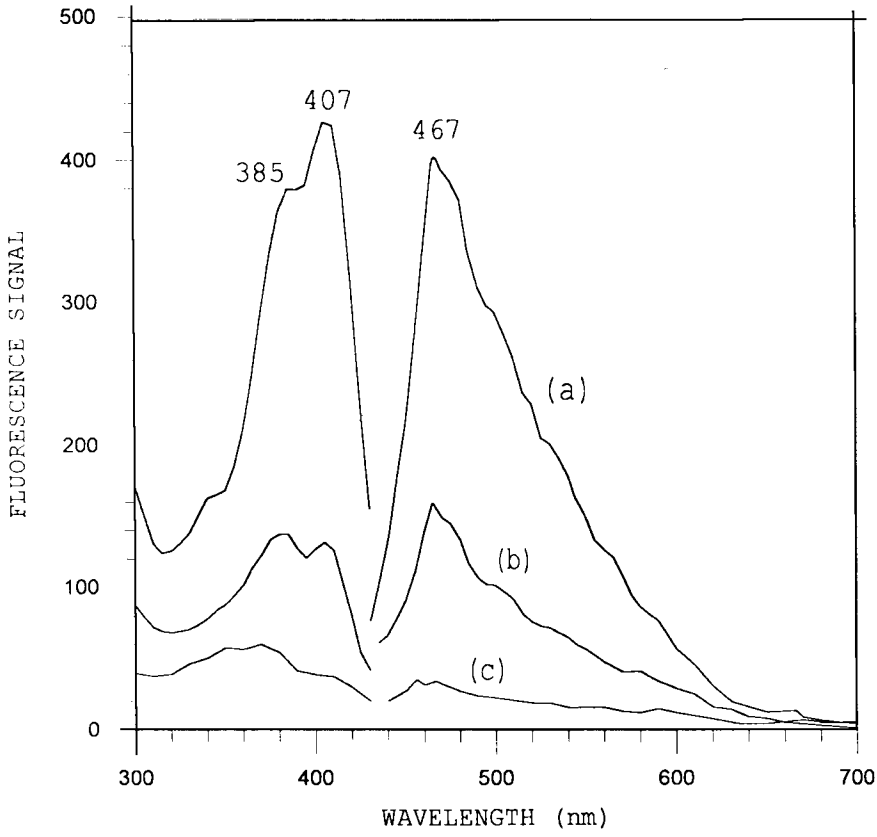

FIG. 1. Excitation and emission fluorescence spectra in 86% DMS (solution-type I) of: (a) TC-Li system, (b) TC-blank, (c) Li-blank. (Instrumental conditions: excitation wavelength, 407 nm; emission wavelength, 467 nm; excitation and emission slits, 5 nm). Spectral-pattern D.

Water (MILLIPORE Q); Methanol (CARLO ERBA); 1-Propanol (PROBUS); Ethanol; 2-Propanol; Acetone; Acetonitrile; N,N–Dimethylformamide -DMF-; 1,4-Dioxan; Ethylenglycol (MERK); Dimethylsulfoxide -DMS-; Pyridine; Tetrahydrofuran -THF-; Glycerine (PANREAC) and Hexamethylphosphotriamide -HMPT- (SIGMA) were used as solvents.

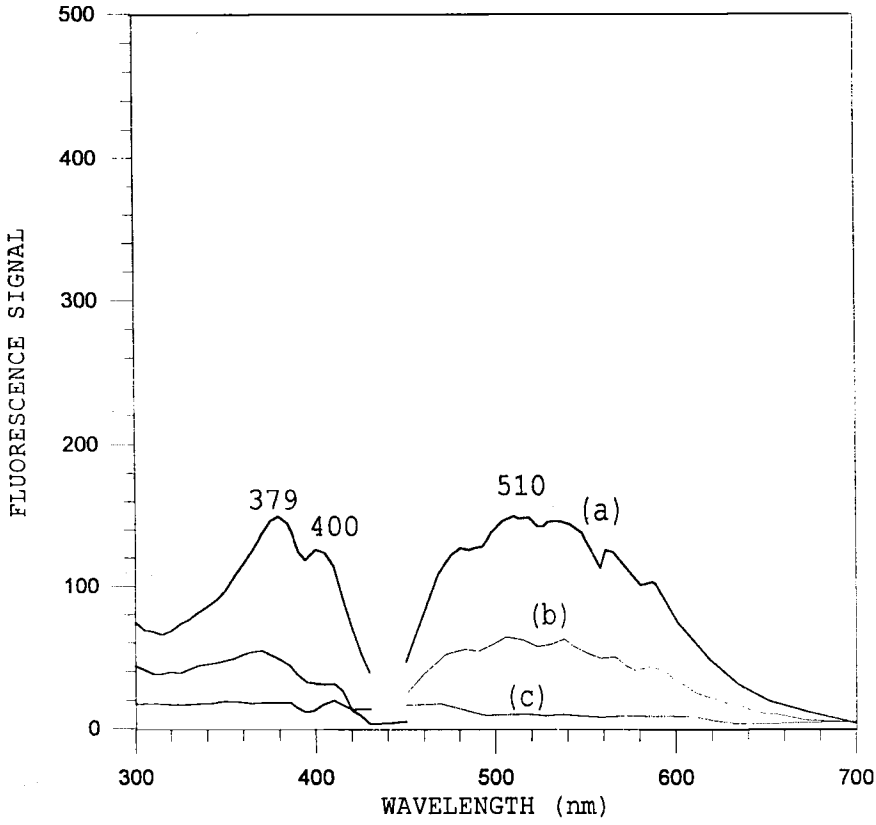

FIG. 2. Excitation and emission fluorescence spectra in 86% ethanol (solution-type I) of: (a) TC-Li system, (b) TC-blank, and (c) Li-blank. (Instrumental conditions: excitation wavelength, 379 nm; emission wavelength, 510 nm; excitation and emission slits, 5 nm). Spectral-pattern E.

General procedure

Two different sets of aqueous/organic solution-types were prepared with several water–miscible solvents and the appropriate amount of the above solutions, containing: Solution–type I: [TC]=10^{-6} M; [NaOH]=6×10^{-2} M; [Li^+]=3×10^{-2} M and 86 % (v/v) of solvent; Solution–type II: [TC]=2×10^{-4} M; [NaOH]=2×10^{-3} M;

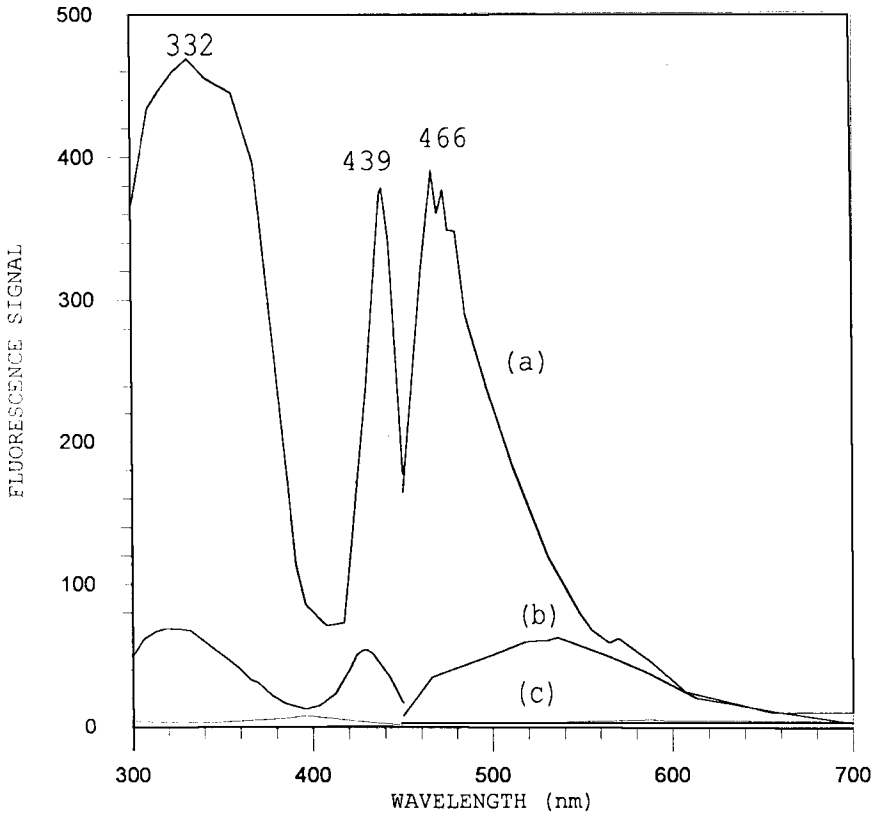

FIG. 3. Excitation and emission fluorescence spectra in 89% DMS (solution-type II) of: (a) TC-Li system, (b) TC-blank, and (c) Li-blank. (Instrumental conditions: excitation wavelength, 439 nm; emission wavelength, 466 nm; excitation and emission slits, 5 nm; attenuation, 3.6%).

$[Li^+]=10^{-2}$ M and 89 % (v/v) of solvent. Similarly, two blanks were prepared in the same conditions for each solution–type: i) the TC–blank, which does not contain lithium ion; and ii) the Li–blank, which does not contain tetracycline.

All the solutions were allowed to stand for 6 minutes and the excitation and emission spectra for each were examined.

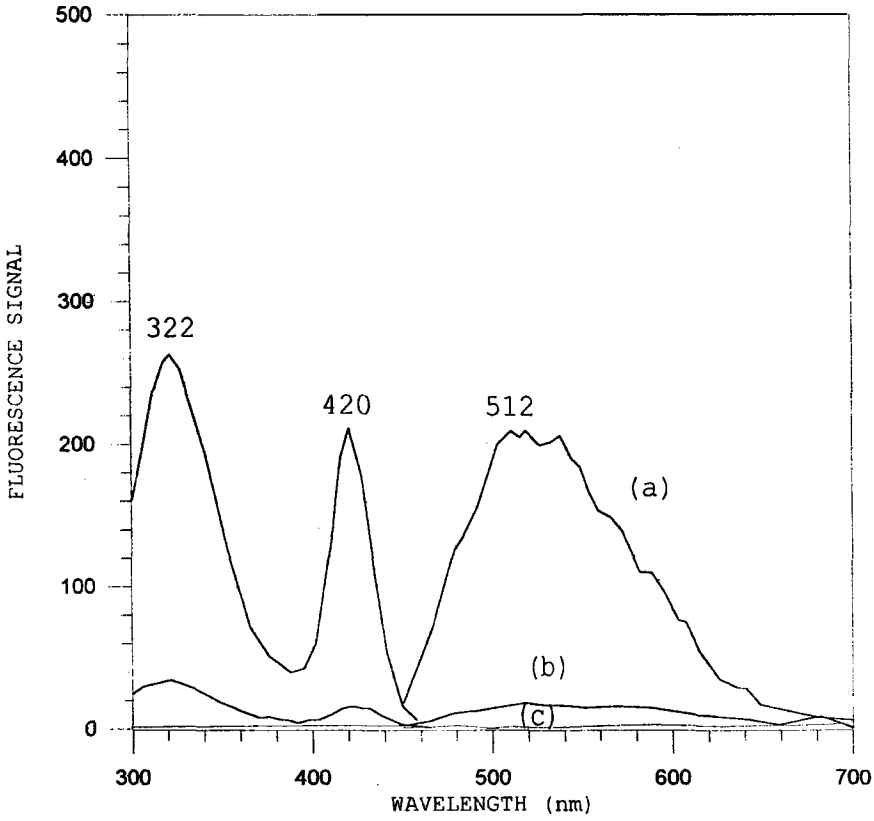

FIG. 4. Excitation and emission fluorescence spectra in 89% ethanol (solution-type II) of: (a) TC-Li system, (b) TC-blank, and (c) Li-blank. (Instrumental conditions: excitation wavelength, 420 nm; emission wavelength, 512 nm; excitation and emission slits, 5 nm; attenuation, 4%).

Results

Table 1 lists both maximum excitation and emission wavelengths, together with fluorescence signals of the TC–Li solutions and SEF^{TC} (SEF^{TC}=TC fluorescence-signal enhancement factor, calculated as Li–TC signal/TC–blank signal), of Solution-type I for each of the solvents previously mentioned. The fluorescence of the Li-

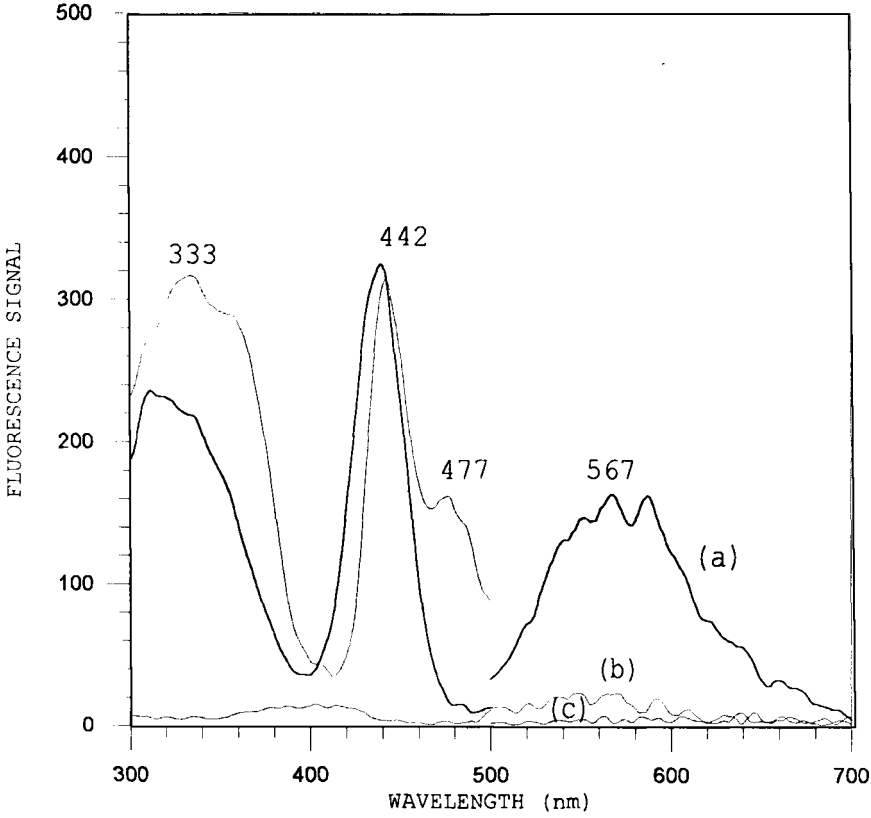

FIG. 5. Excitation and emission fluorescence spectra in 89% DMS (solution-type II) of: (a) TC-Li system, (b) TC-blank, and (c) Li-blank. (Instrumental conditions: excitation wavelength, 477 nm; emission wavelength, 567 nm; excitation and emission slits, 5 nm; attenuation, 30%).

blank is not listed because it is very low and similar in all cases (20-40 fluorescence units).

The fluorescent behaviour of the TC–Li system is different depending on the solvent utilized. For example, Figures 1 and 2 show the excitation and emission spectra (Solution–type I) of two different solvents, DMS and ethanol, in addition to

the corresponding TC–blank and Li–blank for each one. Furthermore, the spectra for DMS (pattern D) and the spectra with ethanol (pattern E) are specified in Table I for each solvent. In these experimental conditions, both the excitation and emission spectra of Li–TC present the same profile as the TC–blank and, in both cases, a similar enhancement of the fluorescence intensity is found: SEF^{TC}_{DMS}=3.25 and $SEF^{TC}_{ethanol}$=2.96.

On the other hand, when the concentrations of TC, Li^+ and NaOH are modified (Solution–type II), a marked change only appears in the excitation spectra (see Figures 3 and 4), and the two spectra present a similar profile, though their respective maximum wavelengths are displaced with respect to each other. The fluorescence–signal enhancement factors are found to be SEF^{TC}_{DMS}=8.38 and $SEF^{TC}_{ethanol}$=13.47.

When the excitation spectrum is recorded at 567 nm of emission wavelength with DMS, a new excitation maximum appears at 477 nm, which is specific to the Li–TC system (SEF^{TC}_{DMS}=9.76), and the corresponding emission spectrum is similar to the one obtained with ethanol, but again, all the spectral maxima are displaced to higher wavelengths (Figure 5). The concentration of NaOH and Li^+ is critical and an increase or decrease in either of these makes the excitation maximum at 477 nm disappear. In Solution–type II conditions, this behaviour is only found with DMS among all the tested solvents.

REFERENCES

1. Schulman S.G., *Molecular Luminescence Spectroscopy. Methods and Applications: Part 1*, ed., Wiley & Sons, New York, 1985, Ch. 2, pp. 49-50 and Ch. 3, p. 267.

2. Georges J., Lanthanide sensitized Luminescence and Application to the Determination of Organic Analytes, Analyst 1996; 118; 1481-6.

3. Elbanowski M., and Makowska B., The Lanthanides as Luminiscent Probes in Investigations of Biochemical Systems, J. Photochem. Photobiol. A: Chem., 1996; 99; 85–92.

4. Cuadros Rodríguez L., Jiménez Linares C., and Román Ceba M., Selective Spectrofluorimetric Determination of Lithium (I) with Quinizarin by Extraction into Tributyl Phosphate, Fresenius J. Anal. Chem., 1996; 356; 320-5.

5. Cuadros Rodríguez L., Jiménez Linares C., and Román Ceba M., Solvent Donicity Influence in the Fluorescence Emission of the Lithium [1,4–Dihydroxyanthraquinones] System. Improvement in the Quantification of Lithium, Anal. Lett., 1997; 30; 847–66.

Date Received: July 29, 1998
Date Accepted: September 20, 1998