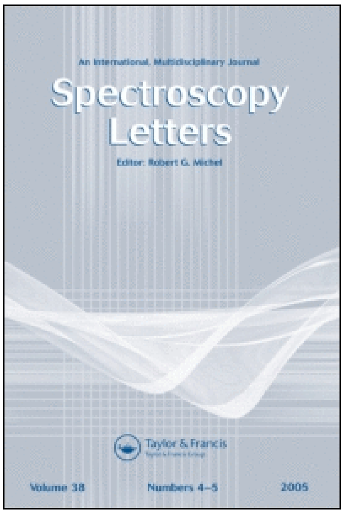

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Fluorescence Quantum Efficiency of Terbium Chelates

V. A. Mode[a]; D. H. Sisson[a]
[a] Lawrence Livermore Laboratory, Livermore, California

To cite this Article Mode, V. A. and Sisson, D. H.(1974) 'Fluorescence Quantum Efficiency of Terbium Chelates', Spectroscopy Letters, 7: 1, 9 — 14

To link to this Article: DOI: 10.1080/00387017408067213

URL: http://dx.doi.org/10.1080/00387017408067213

SPECTROSCOPY LETTERS, 7(1), 9-14 (1974)

FLUORESCENCE QUANTUM EFFICIENCY OF TERBIUM CHELATES

V. A. Mode and D. H. Sisson

Lawrence Livermore Laboratory
Livermore, California 94550

INTRODUCTION

A number of rare earth chelates show bright line emissions. These emissions usually result from the absorption of energy in the broad absorption band of the chelating agent followed by transfer of this energy to an excited state of the central rare earth metal ion. This transfer is followed by emission from one or more of these excited states. The emission spectrum is characteristic of the rare earth ion – discrete, narrow lines – showing no band characteristic of the chelating agent. To understand the absorption, transfer, and emission of light energy in these materials, the efficiency of energy transfer and the quenching processes involved must be determined. A knowledge of the fluorescence quantum efficiency is essential.

A number of methods for measuring the efficiency of fluorescence have been summarized in a review article[1]. Of the several methods proposed, one of the simplest techniques employs a Rhodamine-B fluorescent screen as a quantum counter[2]. The fluorescence efficiency of this material is independent of the wavelength of excitation over the range 220-600 nm. Rhodamine-B effectively integrates the emission of the sample by absorption and then emitts this energy with a constant efficiency at ~610 nm. This technique has made the measurement of quantum efficiencies relatively straightforward if suitable standards can be found.

Bhaumik and Telk have reported[3] the quantum efficiency for a number of rare earth chelates in non-aqueous solutions. The efficiencies observed ranged from 0.1% up to 47%. It was observed that the quantum efficiencies were strongly dependent upon the solvent employed. A number of authors[4-9] have proposed that the fluorescence is quenched by energy transfer to high energy vibrations of the solvent. We have continued this investigation in our laboratory with the hope of understanding the solvent-chelate interaction and the intermolecular energy transfer processes leading to solvent quenching. We report here on the measurement of the fluorescence quantum efficiencies of several terbium β-diketone chelates in nonaqueous solvents.

EXPERIMENTAL

Equipment

A modified Aminco-Bowman SPF spectrophotoflometer[10,11] with a front surface attachment was used for all measurements. A description of the use of this attachment with the Rhodamine-B quantum counter has been published[12]. The cell assembly and filters used for our measurements are shown in Figure 1.

Quinine sulfate was used as the quantum standard of known efficiency. A 5 x 10^{-3} M quinine sulfate solution in 1.0 N sulfuric acid was assumed to have a standard quantum efficiency of 0.508[13].

Because the luminescent volume of the standard and sample solutions were not identical, it was necessary to correct all data for inner-filter effects. A description of this effect and the correction factors to be used has been published[14].

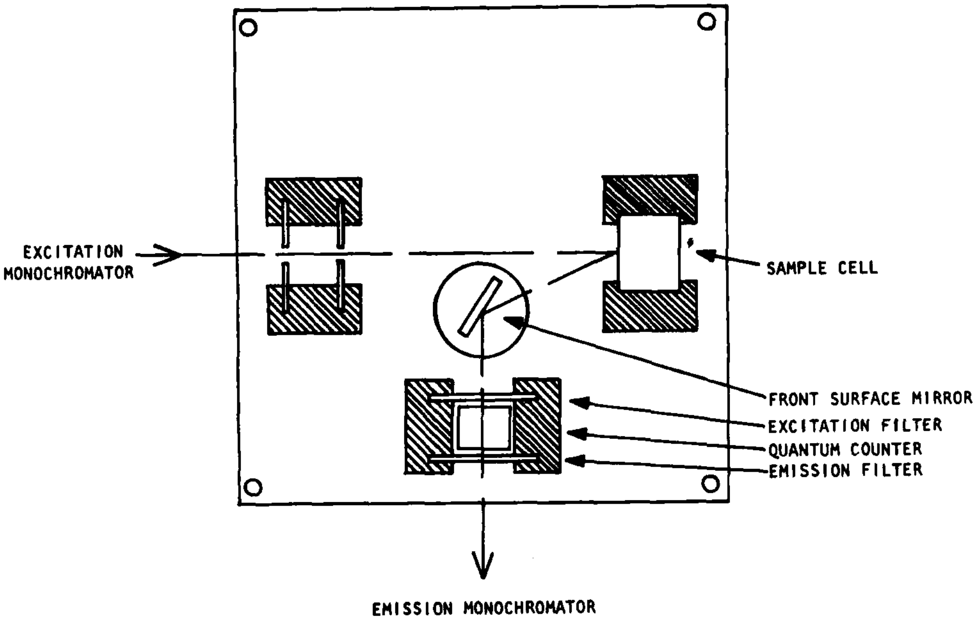

FIG. 1

Front Surface Attachment For Use In An Aminco SPF Spectrophotofluorometer

Sample Preparation

The terbium chelates of 2,2,6,6-tetramethylheptane-3,5 dione (thd) and acetylacetone (AA) were prepared using published techniques and were characterized by elemental analyses and determination of melting points [15-17]. All solvents were MCB "fluorescent grade" reagents, redistilled in our laboratory prior to use.

Previous work[3] has shown that the quantum efficiency of these chelates is not particularly susceptible to quenching by oxygen. We prepared several oxygen-free samples and confirmed this observation.

All other samples were prepared without taking particular efforts to exclude oxygen.

RESULTS AND DISCUSSION

The fluorescence quantum efficiencies of the terbium chelates in selected solvents are shown in Table 1. The highest efficiency measured was approximately 37%. We confirmed the marked solvent dependence previously observed by Bhaumik[3]. Of particular note is the marked decrease in quantum efficiency with increasing methanol concentration.

TABLE 1

Quantum Efficiency of Terbium Chelates in Selected Solvents
$(4.00 \pm 0.10) \times 10^{-4}$ M

	Ethanol	$\frac{\text{Ethanol}}{\text{Methanol}}$ $\frac{3}{1}$	$\frac{\text{Ethanol}}{\text{Methanol}}$ $\frac{1}{9}$	EPA	Hexane	Cyclohexane
$Tb(thd)_3$	23.3	20.1	16.1	29.2	13.8	18.8
$Tb(thd)_3 \cdot DMF$	19.9	17.6	-	26.0	11.1	-
$Tb(AA)_3 \cdot x\ H_2O$	19.5	19.3	-	23.2	36.7	-
$Tb(AA)_3 \cdot 2\ H_2O$		20.0*		14.0*	25.0*	

*From reference 3.

Chrysochoos has shown in a number of studies[18-20] that the presence of higher order vibrational modes may provide a route for the de-excitation of excited states in a number of rare earth ions. He has observed marked quenching of Tb^{+3} in aqueous solutions. He proposes that higher order O-H vibrational bands overlap with the lowest lying triplet state of terbium ion to provide a non-radiative pathway for relaxation.

We have made a preliminary study of the effect of deuteration on the terbium quantum efficiency. These results indicate an enhancement of the quantum efficiency only in the deuterated 9:1 methanol:ethanol solvent (Table 2). Because of the rapid exchange of hydroxyl deuterium in alcohol solutions, it is not clear whether the important mechanism is that of deuteration of the solvent or exchange of the deuterium with the α-hydrogen of the β-diketone.

TABLE 2

Quantum Efficiency of Terbium Chelates in Selected Solvents
$(4.00 \pm 0.10) \times 10^{-4}$ M

	Ethanol		$\frac{\text{Ethanol}}{\text{Methanol}}$ $\frac{3}{1}$		$\frac{\text{Ethanol}}{\text{Methanol}}$ $\frac{1}{9}$	
	-OH	-OD	-OH	-OD	-OH	-OD
$Tb(thd)_3$	23.3	~10	20.1	~10	16.1	~20
$Tb(thd)_3 \cdot DMF$	19.9	~10	17.6	~10	0	~15
$Tb(AA)_3 \cdot x\ H_2O$	19.5	< 1	19.3	~ 3	0	~20

ACKNOWLEDGMENTS

This work was performed under the auspices of the United States Atomic Energy Commission.

REFERENCES

1. J. N. Demas and G. A. Crosby, J. Phys. Chem. 75, 991 (1971).
2. E. J. Bowen, Proc. Royal Soc. (London) 154A, 349 (1936).
3. M. L. Bhaumik and C. L. Telk, J. Opt. Soc. Am. 54, 1211 (1964).
4. M. L. Bhaumik, J. Chem. Phys. 40, 3711 (1964).

5. J. J. Freeman and G. A. Crosby, J. Mol. Spect. 13, 399 (1964).

6. J. L. Kropp and M. W. Windsor, J. Chem. Phys. 42, 1599 (1965).

7. V. L. Ermolaev and E. B. Sveshnikova, Optika and Specto 28, 98 (1970).

8. Y. Haas and G. Stein, J. Phys. Chem. 75, 3677 (1971).

9. Y. Haas and G. Stein, Chem. Phys. Letters 15, 12 (1972).

10. V. A. Mode and R. A. Thomas, Rev. Sci. Inst. 40, 1241 (1969).

11. V. A. Mode, R. A. Thomas, and D. H. Sisson, Rev. Sci, Inst. 41, 1714 (1970).

12. W. H. Melhuish, J. Opt. Soc. Am. 52, 1256 (1962).

13. W. H. Melhuish, J. Phys. Chem. 65, 229 (1961).

14. V. A. Mode and D. H. Sisson, Anal. Chem. (to be published).

15. K. J. Eisentrant and R. E. Sievers, J. Am. Chem. Soc. 87, 5254 (1965).

16. V. A. Mode and D. H. Sisson, Inorg. Nucl. Chem. Letters 8, 357 (1972).

17. One sample of $Tb(AA)_3$ was obtained from Research Organic/Inorganic Chemical Co., Sun Valley, Calif.

18. J. Chrysochoos, Chem. Phys. Letters 14, 270 (1972).

19. J. Chrysochoos, Spectry. Letters 5, 57 (1972).

20. J. Chrysochoos and A. Evers, Spectry. Letters 6, 203 (1973).

Received November 30, 1973

Accepted December 12, 1973