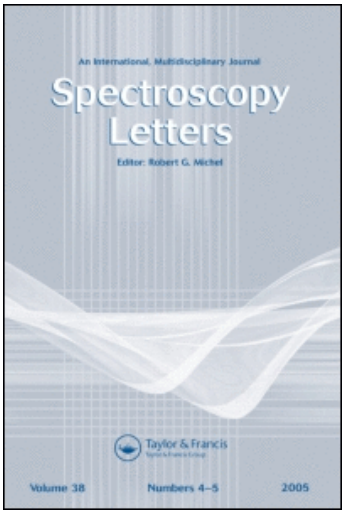

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Some New Laser Dyes - Solvent Effect on QE and Lasing Action

M. R. Padhye[a]; T. S. Varadarajan[a]; A. V. Deshpande[a]
[a] Department of Chemical Technology, University of Bombay, Bombay, India

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SOME NEW LASER DYES - SOLVENT EFFECT ON QE AND LASING ACTION

Key words :- Laser dyes, Quantum efficiency (QE), Fluorescence, Coumarins

M.R. Padhye, T. S. Varadarajan and
A.V. Deshpande,
Department of Chemical Technology,
University of Bombay,
Matunga, Bombay 400019
India

ABSTRACT

With a view to extend the tunability range and maximum output with the coumarin series of dyes, eleven new coumarins differing in the nature of substituents and their positions are synthesized. Two of these are found to be capable of laser action. Optical spectra and quantum efficiencies of these two dyes in various solvents are studied. Correlation between lasing capability, structure of the dye and its optical characteristics is discussed.

INTRODUCTION

Eleven new substituted coumarin derivatives have been synthesized with a view to obtain new laser

active media. Optical absorption and fluorescence emission spectra of these dyes are studied in different solvents with a view to standardise the parameters to make these dyes effective media for laser action.

Out of these eleven dyes, four were capable of luminescence and of these, two showed laser activity. These two were studied in detail with respect to absorption and emission spectra and quantum efficiencies in various solvents. Effect of solvents on the position of the lasing wavelength and on quantum efficiency is discussed.

EXPERIMENTAL :

The synthesis and purification of the new coumarin derivatives are being reported separately. Their purity is tested by IR spectra and also by chromatography. Absorption spectra of these coumarins are recorded on Beckman DK 2 spectrophotometer and fluorescence emission is recorded on Aminco's spectrophotofluorometer. For the precise measurement of quantum efficiencies of these dyes, an experimental set up has been fabricated here. It contains a monochromator and standard photomultiplier together with Spex photon counting system. The photomultiplier is cooled by

using the electro-cooled photomultiplier housing. A point source xenon arc is used as a source of exciting radiation. A freshly prepared MgO is used as an ideal scatterer.

Quantum efficiency of fluorescence, is found by front surface reflection method which is reported to minimise errors in such determination [1-3]. While calculating the quantum efficiency, observed values are corrected for the grating sensitivity and photomultiplier sensitivity. Necessary correction for refractive index is also made. It is hence believed that the values of quantum efficiency are precise absolute values.

Laser action of these dyes was tested by using a Nitrogen laser radiation as pumping radiation and usual transverse cavity with dye solution in one cm cell*

RESULTS:

Fig. I shows the list of dyes synthesized along with their emission character. The first seven dyes are either non-fluorescent or very weakly

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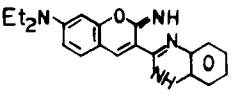
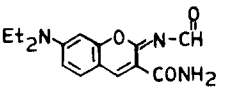
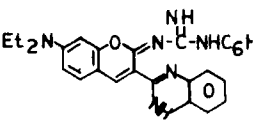
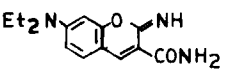
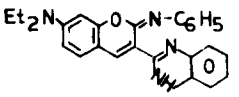
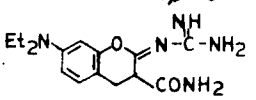
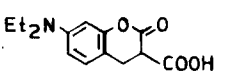
* Laser action of dyes is tested at Spectroscopy Division, B.A.R.C.(India).

NON FLUORESCENT DYES

Dye No.	Chemical Name	Structural Formula
1	2 imino, 3 benzimidazolyl, 7 diethyl amino, coumarin	
2	7 diethyl amino, 3 imido, 2 aldehyde imino, coumarin	
3	7 diethyl amino, 3 benzimidazolyl, 2N phenyl guanidino, imino coumarin	
4	7 diethyl amino, 3 imido, 2 imino, coumarin	
5	7 diethyl amino, 3 benzimidazoly, 2N phenyl imino coumarin	
6	7 diethyl amino, 3 imido, 2N-cynamido, imino coumarin	
7	7 diethyl amino, 3 carboxylic acid, coumarin	

FLUORESCENT DYES

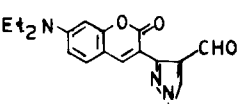
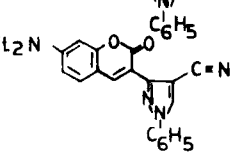
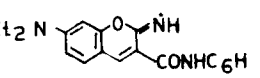
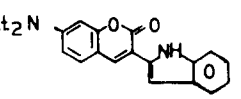
8	7 diethyl amino, 3,3(1 phenyl, 4 aldehydo pyrazolo coumarin	
9	7 diethyl amino, 3,3(1 phenyl, 4 cyno) pyrazolo coumarin	
10	7 diethyl amino, 2 imino, 3 anilyde coumarin	
11	7 diethyl amino, 3 indol coumarin	

Fig. I - List of synthesized Dyes

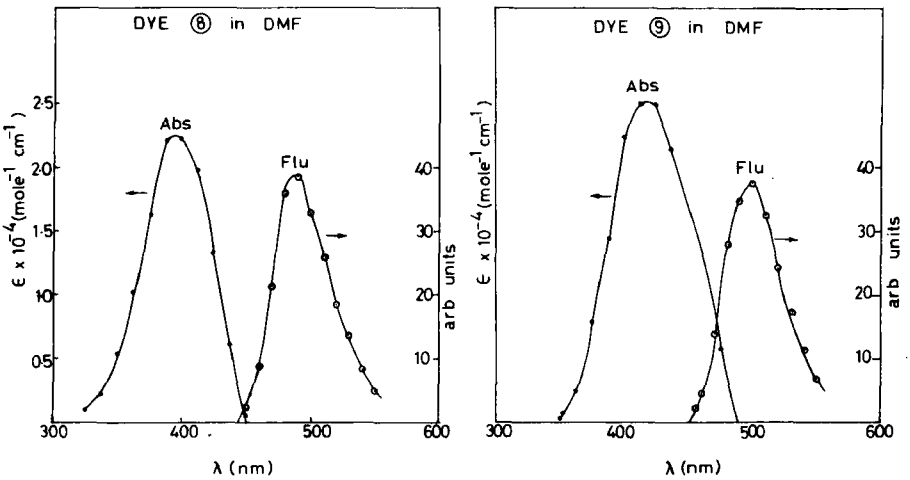


Fig. II - Absorption and Fluorescence spectra of dye No. 8 and 9 in DMF

fluorescent and hence not useful in the context of the present study. Out of the four fluorescent dyes only two, No. 8 and No. 9 are found to give laser action and are studied in detail.

Absorption and emission spectra of these two dyes are recorded in different solvents, viz. Ethanol, Methanol, DMF and Chloroform. Fig. II shows the typical absorption and emission spectra of dye No. 8 and No. 9 in DMF. Fig. III shows the absorption spectra of dye No. 8 and 9 in various solvents.

The emission wavelength as well as the emission intensity are solvent dependent and are

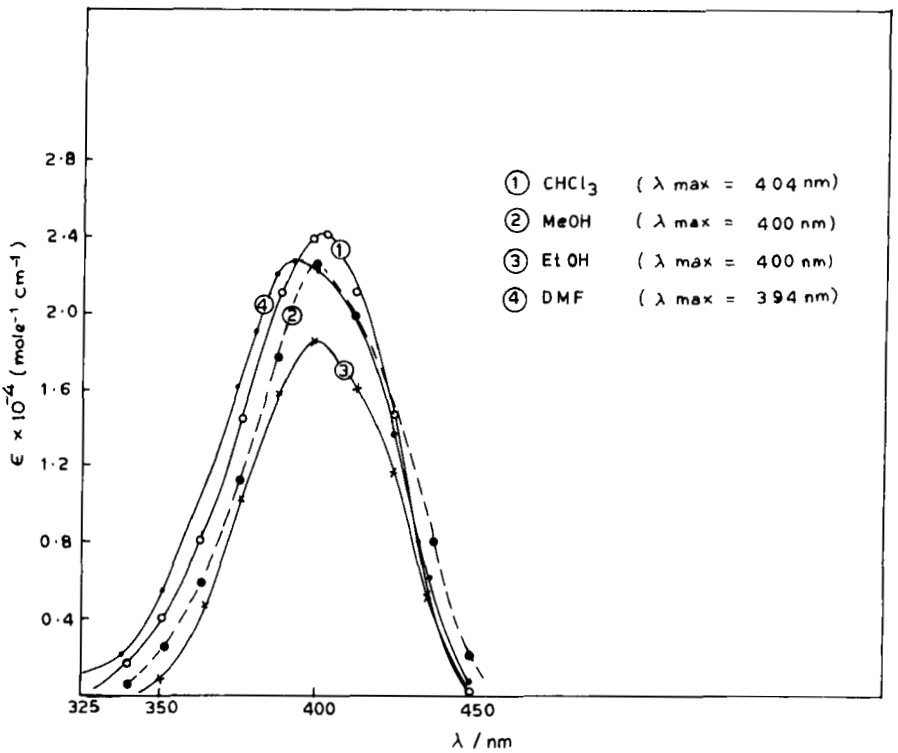


Fig.IIIA[1]- Absorption spectra of dye No.8 in various solvents.

recorded in the table in Fig. IV along with other data for various solvents in case of dyes Nos. 8 and 9.

DISCUSSION:

When the structure of commercial coumarin laser dyes [4-6] are compared with those of the present series, it is observed that in the

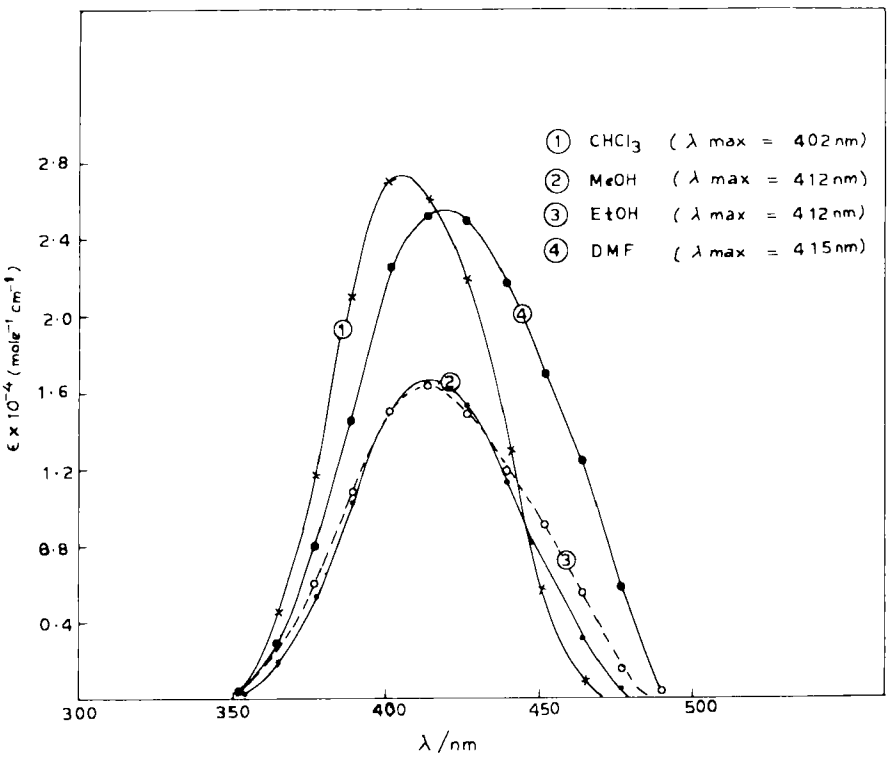
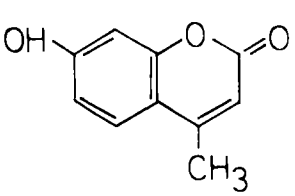


Fig.IIIB4 - Absorption spectra of dye No.9 in various solvents.

present series, there is a more complex substituent at position 3. A typical commercial coumarin structure is as below:



Since the object was to develop dyes with wider

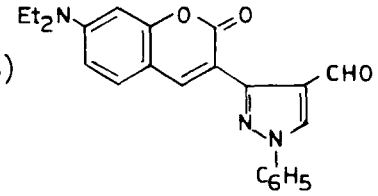
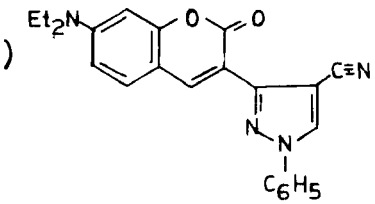
STRUCTURE OF DYE	SOLVENT	$(\frac{\lambda abs}{nm})_{max}$	$(\frac{\lambda exc}{nm})_{max}$	$(\frac{\lambda ems}{nm})_{max}$	QE	Lasing action
8) 	DMF	394	395	487	0·805	Yes
	$CHCl_3$	404	395	482	0·985	Yes
	EtOH	400	395	488	0·660	No
	MeOH	400	395	489	0·260	No
9) 	DMF	415	395	491	0·720	Yes
	$CHCl_3$	402	395	495	0·994	Yes
	EtOH	412	395	500	0·860	No
	MeOH	412	395	500	0·660	No

Fig. IV1 - Spectral characteristics of dye No.8 and 9.

tunability range extending to longer wavelengths, basically it is understood that range of π electron delocalisation ought to increase by more extensive conjugation at position 3, next to 3:4 double bond in the pyran ring. It is obvious that any other position of substitution in the phenyl part is not expected to be as effective since it would lead to cross conjugation. For position 2, conjugation is only effective provided the double bond is next to ring as in imine structure. To complement the effect of increased conjugation, a suitable electron active group in position 7 is expected to be helpful. These considerations were kept in mind while formulating programme of synthesis of the present series of compounds. The deductions though theoretically well founded have practical limitations. All conjugative substituents do not yield required results because of one or more of the following. The substituent may be sterically distorted out of plane of coumarin ring in which case conjugation is not possible, the substituent may have chelating groups which may bring about inter or even-intramolecular hydrogen bonding in which case again, the shift may not be as expected.

This possibly explains why many of the listed compounds are non-fluorescent.

It is also noted that in the case of dyes Nos. 10 and 11 , no laser action is observed because of the low quantum efficiencies in these cases which in DMF are 32 % and 57 % respectively as against 80 % and 72 % in case of dyes nos. 8 and 9. In fact, high quantum efficiency exceeding about 70 % is an essential condition for laser action indicating that radiative $S_1 \rightarrow S_0$ deactivation is the most important or practically exclusive energy dissipation process. Even in the case of dyes Nos. 8 and 9, the laser action is observed only in DMF and chloroform solution but not in alcohols. For dye No. 9 in EtOH, the quantum efficiency is high (86 %) but no laser action is found. This may be due to poor solubility of dye in EtOH. The effect of solvent thus on laser activity seems to arise effectively from changes in quantum efficiency which, in turn, depends on solvent-solute interaction and solubility.

The effect of solvent on dyes Nos. 8 and 9 (Fig. IV) shows that the absorption maximum is at longer wavelength and emission at shorter

wavelength in $CHCl_3$ than in DMF for dye No. 8 which has an aldehyde group whereas it is reverse for dye No. 9 which has a $C \equiv N$ group. In the absence of the hydrogen bonding function this can be explained on the basis of polarizability and the dielectric constant of the solvent. This, however, is not seen to be true for quantum efficiencies which is maximum for chloroform in both dyes. The effect of alcohols is mainly influenced by H bonding for CHO containing dye and dielectric effect for $C \equiv N$ containing dye.

REFERENCES

1. W.H. Melhuish — J. Phys. Chem., 65, 229-235 (1961).
2. J.N. Demas and G.A. Crosby — J. Phys. Chem., 75, 991-1024 (1971).
3. W.H. Melhuish — New.Z.J. Sci. Tech., 37B, 142-149 (1955).
4. F.P. Schafer — Topics in Applied Physics, Vol. 1 Dye Lasers, 2nd Ed. Springer-Verlag, Berlin, Heidelberg, New York (1977)PP. 161-164.

5. D.M. Guthals and J.W. Nibler — Opt. Commun. 29, 322-324 (1979).

6. J.M. Kauffman — Appl. Optics, 19, 3431-3434 (1980).

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