AD-A136 361 PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF COUMARIN LASER DYES IN AMPHIPHILIC MEDIA(U) BOSTON UNIV MA DEPT OF CHEMISTRY G JONES ET AL. 31 OCT 83 TR-6 1/1

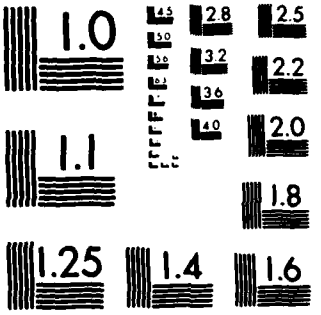
UNCLASSIFIED N00014-79-C-0054 F/G 20/5 NL

END

DATE FILMED

2-84

DTIC




MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(12)

| REPORT DOCUMENTATION PAGE | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|---|
| 1. REPORT NUMBER: Technical Report No. 6 — 2. GOVT ACCESSION NO.: AD-A136361 | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle): Photophysical and Photochemical Properties of Coumarin Laser Dyes in Amphiphilic Media | 5. TYPE OF REPORT & PERIOD COVERED: Technical, 1/1/83-10/31/83 |
| | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s): G. Jones, II, W. R. Jackson, S. Kanoktanaporn, and W. R. Bergmark | 8. CONTRACT OR GRANT NUMBER(s): N00014-79-C-0054 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, Boston University, Boston, Massachusetts 02215 | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 395-609 |
| 11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Eastern/Central Regional Office, 666 Summer Street, Boston MA 02210 | 12. REPORT DATE: October 31, 1983 |
| | 13. NUMBER OF PAGES: 30 |
| 14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) | 15. SECURITY CLASS. (of this report): Unclassified |
| | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |

16. DISTRIBUTION STATEMENT (of this Report)

Reproduction in whole or in part is permitted for any purpose of the United States Government. Approved for public release; distribution unlimited.

DTIC

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DEC 2 7 1983

H

18. SUPPLEMENTARY NOTES

Prepared for publication in the Journal of the American Chemical Society

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Coumarin laser dyes, dye solubilization, aqueous lasing media, photophysics in surfactant or amphiphilic media, laser dye stabilization

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

→ Photophysical properties of coumarin laser dyes solubilized in aqueous detergent or cyclodextrin solutions have been investigated. Dyes appear to be incorporated in hydrated (hydrogen bonded) sites within detergent micelles. Photodegradation is inhibited for detergent solubilized dye. Electron transfer photochemistry is examined by flash photolysis. ←

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601 |

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

A136361

DTIC FILE COPY

# PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF COUMARIN LASER DYES IN AMPHIPHILIC MEDIA

Guilford Jones, II,* William R. Jackson, and Santhi Kanoktanaporn

Department of Chemistry, Boston University, Boston MA 02215

William R. Bergmark*

Department of Chemistry, Ithaca College, Ithaca NY 14850

DTIC COPY INSPECTED

Accession For
NTIS GRA&I
DTIC TAB
Unannounced
Justification
By
Distribution/
Availability Codes
Dist Avail and/or Special
A-1

## Abstract

Photophysical properties of coumarin laser dyes solubilized in aqueous detergent solutions have been investigated including measurement of absorption and fluorescence emission maxima, and fluorescence quantum yields. Results for sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) solutions have been compared with similar findings for organic solvents leading to the conclusion that the sites for dye incorporation in micelles are significantly hydrogen-bonded (hydrated). The inhibition of photochemical decomposition for detergent-solubilized dyes has also been

observed. Electron transfer from bound dye to a water soluble acceptor, methyl viologen, has been investigated by flash photolysis. A preliminary study of dyes solubilized in cyclodextrins is also included.

---

An important objective in studies directed to improvement of the performance of dye lasers is the expansion of options which permit the use of water as solvent for the lasing medium.[1] The attractive features for an aqueous system include the reduction of optical inhomogeneities which are due to thermal gradients which are more pronounced for typical organic solvents. A convenient alternative to the synthesis of dyes with solubilizing groups[2] is the use of common, readily available dyes in conjunction with amphiphiles which serve as solubilizing agents. Beneficial photophysical effects of surfactants on dye laser operation have been suggested[3], and in fact, in the study of rhodamine 6G as the first laser dye, surfactant solutions were employed.[4] In two recent reports the alteration in photophysical properties (enhancement of fluorescence yields) for cyanine dyes solubilized in detergent media[5] or bound to synthetic bilayer membranes[6] has been noted. Increased photostability for cyanines in surfactant solutions was also observed.[5]

As part of an investigation of photochemical and photophysical properties of coumarin laser dyes[7], we have included studies of dye behavior in amphiphilic media. We report here that the coumarins can be solubilized in several different types of aqueous solution. Solubilization leads to noticeable effects on fluorescence spectra and yields of emission; alteration of several photochemical properties has also been observed.

The use of fluorophores as probes of microenvironment for amphiphilic media has been widely studied.[9] Merocyanine-type dyes which display solvatochromic behavior have been employed as "reporters" of the physical properties (microscopic polarity and viscosity) of micelle interiors which provide sites of solubilization.[10] The coumarin dyes of the present study display fluorescence which is remarkably sensitive to medium polarity.[7,8] Our findings therefore permit an evaluation of sites of dye solubilization in amphiphiles with reference to regular shifts in spectral maxima and in emission yields for certain dyes. An unusual sensitivity of the coumarins to the hydrogen bonding properties of a medium is particularly revealing in characterizing the solubilization sites of surfactants. Work will also be reported here involving effects associated with the inclusion of coumarin dyes in cyclodextrins.

## Results and Discussion

Solubilization of dyes in detergent solutions. The solubility of dyes 1- 4 in water was enhanced considerably on addition of surfactants. Increases of 50-100 fold were generally observed as shown for two dyes in Table 1. Assuming the applicability of Poisson statistics and minimal effects of the incorporation of dyes on critical micelle concentrations and aggregation numbers, several characteristics for surfactant solutions could be computed,[22] as shown for 2 (SDS detergent).

concentration of solubilized dye = ca. $9 \times 10^{-4}$ M

concentration of micelles = $4.5 \times 10^{-4}$ M

concentration of solubilized dye in micelle interior = 0.12 M

mean no. of dye molecules per micelle at saturation = 2.0

Although these figures are subject to alteration if solubilization results in changes in surfactant cmc or aggregation number,[23] the values suggest that coumarin dyes at moderate concentration ($10^{-4}$ M) in aqueous detergent solutions will reside almost exclusively in micelle interiors and that dye molecules will be effectively isolated (single occupancy in micelle aggregates) at concentrations $< 2.0 \times 10^{-4}$ M.

Medium effects on dye photophysical properties. Absorption and emission characteristics of coumarins 1-4 are shown in Table 2. The trends are an extension of data previously reported[7,8] which show dramatic effects, particularly on emission maxima and quantum yields. The red shifts of

emission are consistent with relative stabilization in polar media of the planar intramolecular charge-transfer (ICT) coumarin excited state (represented in simplest terms by canonical form 5).[11,7a] The other trend involves the drastic fall-off in quantum yield for 1 and 2 which is less pronounced for structures 3 and 4. The rationale[7a,8] involves the tendency of certain dyes with structures which are unencumbered at the amine moiety (7-position) to undergo facile non-radiative decay in more polar media. This radiationless deactivation is ascribed to conversion of the planar ICT state to a conformer displaying full charge separation (a TICT or twisted intramolecular charge-transfer state, 6).[7,11] The trends in quantum yields for the more rigid dyes which are incapable of achieving the twisted form 6 are also consistent with a more important role for non-radiative decay in more polar media. For these cases (3 and 4) stabilization of the excited state dipole for the emissive ICT state narrows the $S_0 - S_1$ gap.[8]

The significant restoration of coumarin fluorescence which is apparent from the data of Table 1 for SDS detergent solutions vs. water was studied in more detail. Absorption and emission maxima and fluorescence yields for the more polar dyes, 2 and 4, were recorded as a function of surfactant concentration for both anionic (SDS) and cationic (CTAB) surfactants (Tables 3 and 4). As suggested by the solubilization data (Table 1), both detergent media are effective in incorporating dye molecules as shown by the alterations in spectra and the emission yield. Although the absorption maxima do not reveal a clear trend (absorption and emission bands are very broad), the emission wavelengths are clearly blue-shifted as a function of added detergent. The shifts are similar for the two coumarins (4 displays the larger excited state dipole moment or larger solvent red-shift) and

with the use of either of the two surfactants. The latter feature is perhaps noteworthy in that subtle differences in probe behavior have been previously reported for anionic vs. cationic surfactants and for a series of similar probes in a single amphiphilic medium.[14] On the other hand, the merocyanine probes[10] reveal little difference in solubilization sites for SDS and CTAB, indicating minimal influences of the microenvironment having to do with surfactant charge type and head group size. In addition, the relative red-shift (water vs. SDS/water) is comparable for all four dyes, suggesting a similar location in the amphiphile for the four structures.

Solutions of dyes in 50% ethanol provided spectra which were essentially unchanged when saturated with sodium bisulfate suggesting that specific interaction with ionic groups or sensitivity to ionic strength (moderate levels) are unimportant. Notably, the effects of added amphiphile on emission of 2 and 4 are most pronounced for detergent concentrations above the surfactant cmc ($8.5 \times 10^{-4}$ M and $8.0 \times 10^{-3}$ M for CTAB and SDS, respectively[15]). The quenching of coumarin fluorescence by oxygen noted previously[8] is absent for dye solubilized in aqueous surfactants, an effect which has been noted in several studies and ascribed to the low effective concentration of oxygen in micelles.[9]

The extreme sensitivity of 4 to medium polarity (ca. 100 nm red-shift of fluorescence maximum in a range of solvents[7]) provided an opportunity to probe the microenvironment experienced by coumarin molecules incorporated in micelles. A previous correlation of spectral shifts with the $\pi^*$ solvent parameter[16] (for a series of organic solvents not including hydroxylic solvents[7b]), in conjunction with the present data, indicates superficially

that the CTAB and SDS environments are effectively as polar as dimethylsulfoxide ($\varepsilon$ = 47). Although one could identify a reference point of micelle microscopic polarity in terms of dye molecules interacting with a "reaction field"[17] of solvent molecules with effective dipole moment (the property which correlates most readily with $\pi^*$[16,17]) equal to ca. 4.0 D, the solute-micelle interaction involving surfactant chain and head group moieties and intefacial or penetrating water[18] is likely to be far more complex. Other references points are provided by the correlation of dye fluorescence maxima and the hydrogen bonding solvent parameter, $\alpha$,[16,19] previously described[7b] and the general polarity parameter, $E_t(30)$[23] which has been deployed for mixed solvent media.[20] The data which utilize the two solvent parameter scales are shown in Table 4 and the dependences depicted in the Figure.

The satisfactory linear correlation (r = 0.97) with alpha is consistent with the stabilization of dye excited state dipoles, specifically through the donation of hydrogen bonds.[7b,19] Noticeably, hydrogen bonding solvents are generally more effective than the most polar of the non-hydrogen bonding solvents. Although the correlation with the $E_t(30)$ parameter shows typical curvature,[20] the regular response of dye fluorescence frequency is likewise indicative of a significant role for water molecules in excited state stabilization. The results for CTAB and SDS detergent media (Figure) are consistent with the already established notion that neutral (but moderately polar) solutes such as the coumarins experience a micelle microenvironment which is highly polar due to an orientation near the micelle surface and/or the effects of water molecules which enter the micelle interior.[9,13,14,18,21] The location of CTAB and SDS data

points at the polar extreme[5] of the $\pi^*$ scale (indicating a microscopic polarity that only the most polar of non-hydroxylic moieties could duplicate) and the $\alpha$ scale suggest that coumarin 4 and presumeably the other similar structures, are substantially hydrated (hydrogen bonded) when solubilized.

Flash photolysis results below will give some indication that dye molecules are not incorporated in micelles at their outermost surface. Analysis continues with the usual qualifications that a fluorescence probe is at best a reporter of solubilization sites averaged over a host of residences within a dynamic micelle structure and that the host fluorophore is a benign presence in micelle interiors (e.g., does not disrupt organizate structure by providing a special attraction for water). One concludes therefore from the fluorescence data for 4 that water penetration well beyond the interfacial region[19] resulting in a relatively "remote" yet hydrophilic site for solubilization of 4 is important. Given the short lifetimes of coumarin singlets (< 5 ns)[7a,8], little opportunity is provided for rearrangement of micelle structure or probe relocation during the period of the fluorescent state; nevertheless, considerable stabilizatcn of the large excited state dipole[22] is provided by the water-rich micelle environment.

Quantum yields of fluorescence for 2 were useful as a probe of micelle microviscosity. The strength of emission for this dye is known to respond moderately to macroscopic solvent viscosity as well as polarity. The data, including values reported previously [7,8] are shown in Table 7. The sharp reduction in emission yield in more polar and hydroxylic media is partially

offset for more viscous solutions. The important comparison involves the media capable of delivering hydrogen bonds (the alcohols and aqueous surfactant solutions) in which the fluorescence maxima reveal a not too dissimilar microscopic polarity. Within these examples, the fluorescence yields, on the other hand, reveal that SDS and CTAB surfactants display an effective viscosity clearly greater than water, well short of the value for glycerol, but similar to the result for ethylene glycol ($\eta$ = 26 cP). Another study employing a merocyanine probe produced a similar range of values (23 - 34 cP) for several detergents.[10a] Thus, in contrast to the medium-induced red shifts of emission which indicated the extent of micelle relaxation around (and stabilization of) a moderately polar (Franck-Condon) excited state (i.e. 5), the signature of viscosity is one of resistance to further relaxation involving significant rotatory motion leding to the fully charged zwitterionic state (6), presumeably due to a viscous drag imposed by surfactant structure.

Photochemistry of dyes in surfactant media. Steady photolysis of aqueous SDS and CTAB solutions of the dyes revealed a significant resistance to photodegradation when comparison was made with photochemical results for non-hydroxylic solvents. Dealkylation of 2 (an important photodecomposition path for 1 and 2[7c]), having a quantum yield for dilute solutions of dye in acetonitrile or chloroform of ca. $10^{-4}$, was reduced in importance in SDS and CTAB solutions by at least a factor of ten for parallel irradiations at 320-380 nm. Destruction of 4[7c] was likewise inhibited

for detergent media relative to acetonitrile.

The origin of the retardation of photodecomposition for surfactant solutions could be the result of the hydrogen bonding by micellar water which is indicated by the probe data (photodegradation is retarded in alcohols[7c]). On the other hand, it may specifically result from the isolation of dye molecules in micelles which prohibits bimolecular self quenching which has been shown to be important.[7c,23] From the solubilization data it appears safe to conclude that bimolecular singlet reaction is excluded by micelle solubilized dye at concentrations much below 0.1 mM (even though a residual photodegradation is important at these levels for homogeneous solutions), assuming that the relatively slow exit from micelles (microseconds) is required.[8]

Flash photolysis experiments were conducted to determine the nature of any long lived photochemical intermediates and to investigate the interaction of solubilized dye with extramicellar reagents. On photolysis with a conventional flash apparatus (Xe lamp, flash duration ca. 30 μs FWHM) the triplet of 1 ($\lambda_{max}$ = 625 nm, $\tau$ = 120 μs) which can be observed in acetonitrile[7c] or ethanol[24], is absent for 0.1 mM solutions of 1 in argon-purged water. A broad visible absorption (~ 700 nm), suggestive of the solvated electron[25], was detectable. For 1 in 10 mM SDS, the broad absorption was barely in evidence, but the transient (625 nm) assigned to the triplet appeared in low yield (ca. 10% of the absorbance for acetonitrile solutions at 100 μs following the flash).

To study quenching phenomena, the well known electron transfer agent, methyl viologen ($MV^{2+}$), 2b was added to aqueous solutions of 1 (solubility

limit for the coumarin = ca. 0.01 mM). Under these conditions, the dominant transient was the methyl viologen radical, $MV^{+\cdot}$ ($\lambda_{max}$ = 395 and 600 nm) whose absorption was fully developed in the microsecond range and which decayed with a half-life of a few milliseconds. Significantly, this transient was only weakly detected for 1 in 10 mM SDS solutions (~ 10% of the absorption found for 1 and $MV^{2+}$ in water).

The flash photolysis results are consistent with the following features. Incorporation of 1 in SDS micelles "protects" to some extent the dye from the dominant non-radiative decay paths of its singlet state (rotatory decay, 5 - 6,[8] and the presumed photoionization yielding the solvated electron[27] which are important for aqueous solutions (i.e., a modest yield of triplets is thus permitted[29]). Likewise, electron transfer from 1 to $MV^{2+}$ which is most likely the result of trapping solvated electrons, is inhibited (although not excluded) on incorporation of 1 into SDS aggregates. The reduced tendency of triplet 1 to undergo electron transfer with methyl viologen also indicates that location of dye molecules in a region dominated by micelle head groups is less important since it has been shown that $MV^{2+}$ is closely associated with the interfacial region of SDS organizates and may be able to penerate micelles to some degree.[30]

Photophysical properties of dyes in aqueous cyclodextrin solutions. The coumarin dyes were readily solubilized in cyclodextrin[31] solutions, although some important dependences were observed. α-Cyclodextrin (six

linked glucose units) was ineffective in raising solubility for any of the dyes, whereas 1.0 mM solutions of 1 and 2 were readily obtained for aqueous 10 mM β-cyclodextrin. The more rigid structure of 4 appeared to be an inhibiting influence such that only the larger γ-cyclodextrin (eight linked glucose units) was successful in incorporating the dye (0.006 mM).

Absorption and emission data for the cyclodextrin-coumarin complexes are shown in Table 8. Significantly red-shifted absorption and emission were observed, suggesting again an hydroxylic environment. Notably, for cyclodextrin solutions the fluorescence maxima are blue-shifted relative to the results for a pure aqueous environment and reminiscent of the hydrophobic interaction indicated by the data for surfactants. On comparing spectral data for the dyes incorporated in cyclodextrins with findings for the surfactant media, one concludes that a slightly more hydrophobic environment is provided by the inclusion reagents relative to the surfactants. By comparison, the detergent media were more effective than cyclodextrins in sequestering a cationic amphiphilic probe incorporating the indole fluorophore, due apparently in part to the incomplete complexation of the probe in the cyclodextrin media.[21] A number of groups have reported fluorescence enhancement due to guest-host interaction in cyclodextrins.[21] To the extent that our fluorescence yield data are reliable, this result is not repeated for the coumarins (Table 7).

Flash photolysis experiments were not conducted extensively for these media, but one result is revealing. Flashing a 0.1 mM solution of 1 in 10 mM β-CD in the presence of 1.0 mM $MV^{2+}$ resulted in formation of the viologen radical in about the same yield as that obtained on photolyzing a

solution of dye and viologen in water (i.e., net electron transfer is more effective for an inclusion complex of the dye than for dye suspended in a micellar aggregate). If monophotonic ionization is an important non-radiative decay path for the coumarins incorporated in cyclodextrin cavities, (i.e., the bath of water molecules is effectively at closer range for the cyclodextrins), then the low yields of emission would be accounted for. We cannot at this stage exclude other photochemical paths that may be important for the inclusion compounds, although we note that the dyes are exceedingly photostable in these media (dye lifetimes comparable to the longest found for either surfactant solutions or with alcohol solvents).

## Summary

The enhancement of solubility of coumarin laser dyes in water (>500 fold) by SDS and CTAB surfactants and cyclodextrins has been demonstrated. The dyes serve as fluorescence probes of the interiors of surfactant micelles or cyclodextrin cavities with the fluorescence wavelength shifts indicating specifically an environment with strong hydrogen bonding characteristics (a substantial level of hydration). Enhancement of fluorescence yield (ca. three-fold) for dyes in surfactant media relative to aqueous solutions is also observed. The coumarins display a higher degree of photostability in the amphiphilic media relative to the general behavior in organic solvents and a resistance to oxygen quenching of fluorescence. A reduced tendency to participate in electron transfer with a reagent relegated to the aqueous phase has also been observed for detergent-solubilized dye.

## Experimental Section

Dyes 1 - 4 were laser grade materials obtained either from Eastman Kodak (coumarins 1, 35, 102, and 153, respectively) or from Exciton Chemical Co. (coumarins 460, 480, and 540A). The dyes were checked for purity by tlc (silica, ethyl acetate/hexane) and in most cases used as received. In some cases dyes were recrystallized from heptane or methanol/water. Compound 2 was prepared by the method previously reported[10], and purified by vacuum sublimation and recrystallization from methanol. Spectroquality organic solvents were used (MCB "omnisolv") and water was triply distilled. Sodium dodecyl sulfate (SDS, Aldrich) and cetyltrimethylammonium bromide (CTAB, P and B) were purified by recrystallization from methanol or ethanol. Cylodextrins were purified by recrystallization from water. SDS, CTAB, and cyclodextrin aqueous solutions were free of fluorescent impurities. Quinine sulfate dihydrate (Aldrich) was purified by recrystallization from water.

Emission spectra were recorded on a Perkin-Elmer MPF 44-A fluorescence spectrophotometer equipped with a spectrum correction unit and using quartz cells. Dye concentrations of $10^{-5}$ or less were generally employed for experiments which generated absorption and emission maxima, except for detergent solutions where slightly higher concentrations were used (1-5 x $10^{-5}$ M, appreciably above the level of solubility of dye in pure water). Fluorescence quantum yields were determined using quinine sulfate as the reference ($\phi_f$ = 0.55) with refractive index and differential absorption

corrections. For these measurements dilute samples (ca. $10^{-5}$ M, O. D., max. = 0.2) were used with excitation at or near the absorption maximum as described.[8] Fluorescence intensities were recorded for air saturated and argon purged samples and corrections applied so that all values reported correspond to yields appropriate for oxygen free solutions. Absolute values of fluorescence yield are less certain for aqueous surfactant solutions where higher concentrations of dye were generally used to insure incorporation of dye in surfactant micelles.

Flash photolysis apparatus has been described previously (Xenon flash lamp, with ca. 35 s flash FWHM, 22 cm Pyrex cell, argon-purged $10^{-5}$ M solutions).[33] Photochemical products were monitored for 1 and 2 by glc as reported.[7c] Solubilities of dyes in surfactant solutions were obtained after vigorous stirring of mixtures of excess dye with detergent solutions (48 hr). Absorbances of filtered solutions were compared with similar aqueous solutions prepared without surfactant. Concentrations were calculated using extinction coefficients determined for methanol solutions.

Acknowledgements. Support of this research by the U. S. Office of Naval Research is gratefully acknowledged. We also thank Matthew Ziak and Chol-yoo Choi for technical assistance.

References

1. Drexhage, K. H.; in "Dye Laser: Topics in Applied Physics," vol 1, Schafer, F. P., ed., Springer-Verlag, N. Y., 1973.

2. a. Lee, L. A.; Robb, R. A. IEEE J. Quantum Elect. 1980. QE-16, 777; b. Drexhage, K.H.; Erikson, G.R.; Hawks, G.H.; Reynolds, G.A. Optics Commun. 1975. 15, 339.

3. Wallace, S. K.; Thomas, J. K. Radiation Res. 1973. 54, 49.

4. Peterson, D. G.; Tuccio, S. A.; Snavely, B. B. Appl. Phys. Lett. 1970. 17, 245.

5. Humphry-Baker, R.; Gratzel, M.; Steiger, R. J. Am. Chem. Soc. 1980. 102, 847.

6. Nakashima, N.; Kunitake, T. J. Am. Chem. Soc. 1982. 104, 4261.

7. a. Jones, G., II; Jackson, W. R.; Halpern, A. M. Chem. Phys. Lett. 1980. 72, 391. b. Jones, G., II; Jackson, W. R.; Kanoktanaporn, S.; Halpern, A. M. Optics Commun. 1980. 33, 315. c. Jones, G., II; Bergmark, W. R. submitted.

8. Jones, G., II; Choi, C.-Y.; Jackson, W. R.; Bergmark, W. R. submitted.

9. Turro, N. J.; Gratzel, M.; Braun, A. M. Angew. Chem. Int. Ed. Engl. 1980. 19, 675.

10. a. Law, K. Y. Photochem. and Photobiol. 1981. 33, 799; b. David, C.; Szalai, E.; Baeyens-Volant, D. Ber. Bunsenges Phys. Chem. 1982. 86, 710; c. Miach, M. J.; Shah, S. S. J. Org. Chem., 1979. 44, 3252.

11. Almgren, M.; Grieser, F.; Thomas, J. K. J. Am. Chem. Soc., 1979. 101, 279.

12. Mukerjee, P. Pure Appl. Chem. 1980. 52, 1317.

13. Grabowski, Z. R.; Rotkiewica, K.; Siemairczuk, A.; Cowley, D. J.; Baumann, W. Nouveau J. Chim. 1979. 8, 443

14. a. Winkle, J. R.; Worsham, P. R.; Schanze, K. S.; Whitten, D. G. J. Am. Chem. Soc. 1983. 105, 3951; b. Otruba, J.P.; Whitten, D.B. ibid. 1983. 105, 6503; c. Ramachandran, C.; Pyter, R.A.; Mukerjee, P. J. Phys. Chem. 1982. 86, 3198.

15. Mukerjee, P.; Mysels, K. Critical Micelle Concentrations of Aqueous Surfactants, National Bureau of Standards, National Standard Reference Data System, 1971.

16. a. Abboud, J. L. M.; Kamlet, M. J.; Taft, R. W. Prog. Phys. Org. Chem. 1981. 13, 485; b. Kamlet, M.J.; Abboud, J.M.; Abraham, M.H.; Taft, R.W. J. Org. Chem. 1983. 48, 2877.

17. Abboud, J. L. M.; Taft, R. W. J. Phys. Chem. 1979. 83, 412.

18. Menger, F. M. Accts. Chem. Res. 1979. 12, 111.

19. Taft, R. W.; Kamlet, M. J. J. Am. Chem. Soc., 1976. 98, 2886.

20. Langhals, H. Angew. Chem. Int. Ed. Engl. 1982. 21, 724.

21. Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems," Academic Press: New York, 1975; chp 3.

22. Dipole moments of 10-15 D for ICT-type excited species similar to 5 have been determined theoretically or by electrooptical methods.[18]

23. Several measurements of fluorescence intensity for 4 (around 0.1 mM) as a function of the concentration of the dye in 10 mM SDS have been made. Very high concentrations of dye which would allow use of front-face illumination could not be achieved. An accurate quantitative study over a considerable concentration range was not possible due to large corrections required for inner filter effects and differential absorption. Nonetheless, self quenching was not important for 0.01 mM dye but was onset at 0.1 mM 4 where double occupancy of micelles begins to have some proba-

bility.

24. Dempster, D. N.; Morrow, T.; Quinn, M. F. J. Photochem. 1973/74, 2, 29. Dempster, D. N.; Morrow, T.; Quinn, M. F. J. Photochem. 1973/74. 2, 29.

25. Hart, E. J.; Anbar, M. "The Hydrated Electron," Wiley Interscience: New York, 1970.

26. Kalyanasundaram, K. Coord. Chem. Rev. 1982, 159.

27. Viologen reduction proceeds under conditions in which direct singlet quenching is not important and (in water) where dye triplets are either not formed appreciably or have very short lifetimes ( < 1 μ sec) (again making direct excited state quenching by $MV^{2+}$ less likely). We have not determined whether, under flash photolysis conditions, photoionization is mono- or biphotonic.[28]

28. For recent refs to photoionization in micelles, see Escabi-Perez, J. R.; Romero, A.; Lukac, S.; Fendler, J. H. J. Am. Chem. Soc., 1979, 101, 2233, and Narayana, P. A.; Li, A. S. W.; Kevan, L. J. Am. Chem. Soc., 1982, 104, 6502

29. A triplet yield of 0.006 has been reported for 1 in ethanol.[24]

30. a. Whitten, D.B.; Russell, J.C.; Schmehl, R.H. Tetrahedron, 1982,

38, 2455; b. Foreman, T. K.; Sobol, W. M.; Whitten, D. G. J. Am. Chem. Soc., 1981, 103, 5333.

31. Bender, M. L.; Komiyama, M. "Cyclodetrin Chemistry" Springer-Verlag: New York, 1977.

32. Turro, N. J.; Okubo, T.; Chung, C. J. Am. Chem. Soc. 1982, 104, 3954.

33. Carpari, G.; Hughes, R. G.; Endicott, J. F.; Hoffman, M. Z.; J. Am. Chem. Soc. 1970, 92, 6801.

Figure caption

Figure. Fluorescence maxima ($\nu_f$) for 4 as a function of solvent parameters, α, for the series of protic solvent (Δ) and $E_t(30)$ for dioxane/water mixtures(○) (data from Table 5).

Table 1. Solubilities of dyes in aqueous media

| Medium | [2],M | [4],M |
|---|---|---|
| $H_2O$ | $6 \times 10^{-6}$ | $2 \times 10^{-6}$ |
| $H_2O$ + 9mM CTAB | $4 \times 10^{-4}$ | $7 \times 10^{-5}$ |
| $H_2O$ + 40 mM SDS | $9 \times 10^{-4}$ | $1 \times 10^{-3}$ |

Table 2. Absorption and fluorescence maxima and fluorescence quantum yields for coumarin dyes in various media[a]

| | | $CHCl_3$ | $CH_3CN$ | $CH_3CH_2OH$ | 50% $CH_3CH_2OH$ | $H_2O$ | SDS[b] |
|---|---|---|---|---|---|---|---|
| 1 | $\lambda_a$ | 361 | 366 | 373 | 381 | 380 | 375 |
| | $\lambda_f$ | 421 | 433 | 451 | 454 | 456 | 449 |
| | $\phi_f$ | 1.01 | 1.03 | 0.73 | 0.27 | 0.055 | 0.11 |
| 2 | $\lambda_a$ | 387 | 398 | 400 | 412 | 406 | 406 |
| | $\lambda_f$ | 466 | 501 | 509 | 523 | 528 | 513 |
| | $\phi_f$ | 0.92 | 0.064 | 0.078 | 0.030 | 0.010 | 0.030 |
| 3 | $\lambda_a$ | 382 | 380 | 387 | 396 | 396 | 394 |
| | $\lambda_f$ | 433 | 447 | 473 | 477 | 489 | 480 |
| | $\phi_f$ | 1.00 | 0.91 | 0.95 | 1.02 | 0.66 | 0.68 |
| 4 | $\lambda_a$ | 403 | 418 | 421 | 425 | 430 | 422 |
| | $\lambda_f$ | 483 | 521 | 531 | 542 | 549 | 540 |
| | $\phi_f$ | 0.80 | 0.56 | 0.38 | 0.26 | 0.12 | 0.29 |

[a]Spectral data, $\lambda_{max}$, in nm. Fluorescence yields for argon-purged solutions.

[b]$10^{-2}$ M aqueous sodium dodecylsulfate.

Table 3. Photophysical properties of 2 in water as a function of detergent concentration

| Detergent, M x $10^2$ | $\lambda_a$ | $\lambda_f$ | $\phi_f$ |
|---|---|---|---|
| cetyltrimethylammonium bromide (CTAB) | | | |
| — | 406 | 535 | .010 |
| 0.25 | 410 | 532 | .009 |
| 0.56 | 413 | 520 | .021 |
| 2.1 | 408 | 520 | .027 |
| 3.4 | 413 | 519 | .025 |
| 5.1 | 413 | 515 | .024 |
| sodium dodecylsulfate (SDS) | | | |
| — | 410 | 539 | .010 |
| 0.19 | 408 | 521 | .009 |
| 1.0 | 410 | 518 | .031 |
| 3.2 | 407 | 518 | .032 |
| 6.4 | 406 | 513 | .035 |

Table 4. Photophysical properties of 4 in water as a function of detergent concentration[a]

| Detergent, M x $10^2$ | $\lambda_a$ | $\lambda_f$ | $\phi_f$ |
|---|---|---|---|
| cetyltrimethylammonium bromide (CTAB) | | | |
| --- | 430 | 553 | .11 |
| 0.13 | 428 | 554 | .28 |
| 1.1 | 434 | 543 | .58 |
| 3.0 | 433 | 544 | .59 |
| 7.0 | 432 | 542 | .61 |
| sodium dodecylsulfate (SDS) | | | |
| --- | 420 | 553 | .12 |
| 0.20 | 425 | 543 | .24 |
| 0.83 | 427 | 540 | .33 |
| 4.2 | 422 | 541 | .29 |
| 8.2 | 410 | 540 | .27 |

[a] [4] = $5.0 \times 10^{-5}$ M ($2.0 \times 10^{-6}$ M in $H_2O$)

Table 5. Absorption and emission data for 4 and solvent parameters for for alcohols and dioxane/water mixtures[a]

| Solvent | Parameter | $\lambda_a$ | $\lambda_f$ | $\nu_f$ |
|---|---|---|---|---|
| alcohols | $\alpha$[b] | | | |
| tBuOH | 0.62 | 416 | 513 | 19.50 |
| iPrOH | 0.78 | 420 | 522 | 19.15 |
| nBuOH | 0.79 | 420 | 527 | 18.97 |
| nPrOH | 0.81 | 421 | 528 | 18.94 |
| ethanol | 0.85 | 421 | 531 | 18.83 |
| methanol | 0.98 | 422 | 537 | 18.63 |
| water | 1.13 | 420 | 547 | 18.30 |
| CTAB (.03 M) | | 433 | 544 | 18.38 |
| SDS (.04 M) | | 422 | 541 | 18.48 |
| % (V/V) dioxane | $E_T(30)$ | | | |
| 100 | 36.0 | 405 | 494 | 20.24 |
| 90 | 46.7 | 414 | 526 | 19.01 |
| 80 | 49.0 | 419 | 534 | 18.73 |
| 70 | 50.9 | 422 | 540 | 18.52 |
| 60 | 52.3 | 426 | 543 | 18.41 |
| 50 | 53.6 | 429 | 546 | 18.31 |
| 40 | 55.6 | 432 | 549 | 18.21 |
| 30 | 57.2 | 434 | 551 | 18.15 |

[a]Absorption ($\lambda_a$) and fluorescence ($\lambda_f$) maxima in nm, frequencies in kK.

[b]Ref. 16

Table 6. Spectral data and quantum yields of fluorescence for 2 as a function of medium viscosity (25°)

| Solvent | η,cP | $\lambda_a$ | $\lambda_f$ | $\phi_f$ |
|---|---|---|---|---|
| cyclohexane | 0.98 | 376 | 433 | 1.04 |
| ethyl acetate | 0.43 | 392 | 479 | 0.84 |
| acetonitrile | 0.38 | 398 | 501 | 0.064 |
| water | 0.89 | 406 | 528 | 0.010 |
| ethylene glycol | 26. | 409 | 518 | 0.030 |
| glycerol | 945. | 413 | 524 | 0.16 |

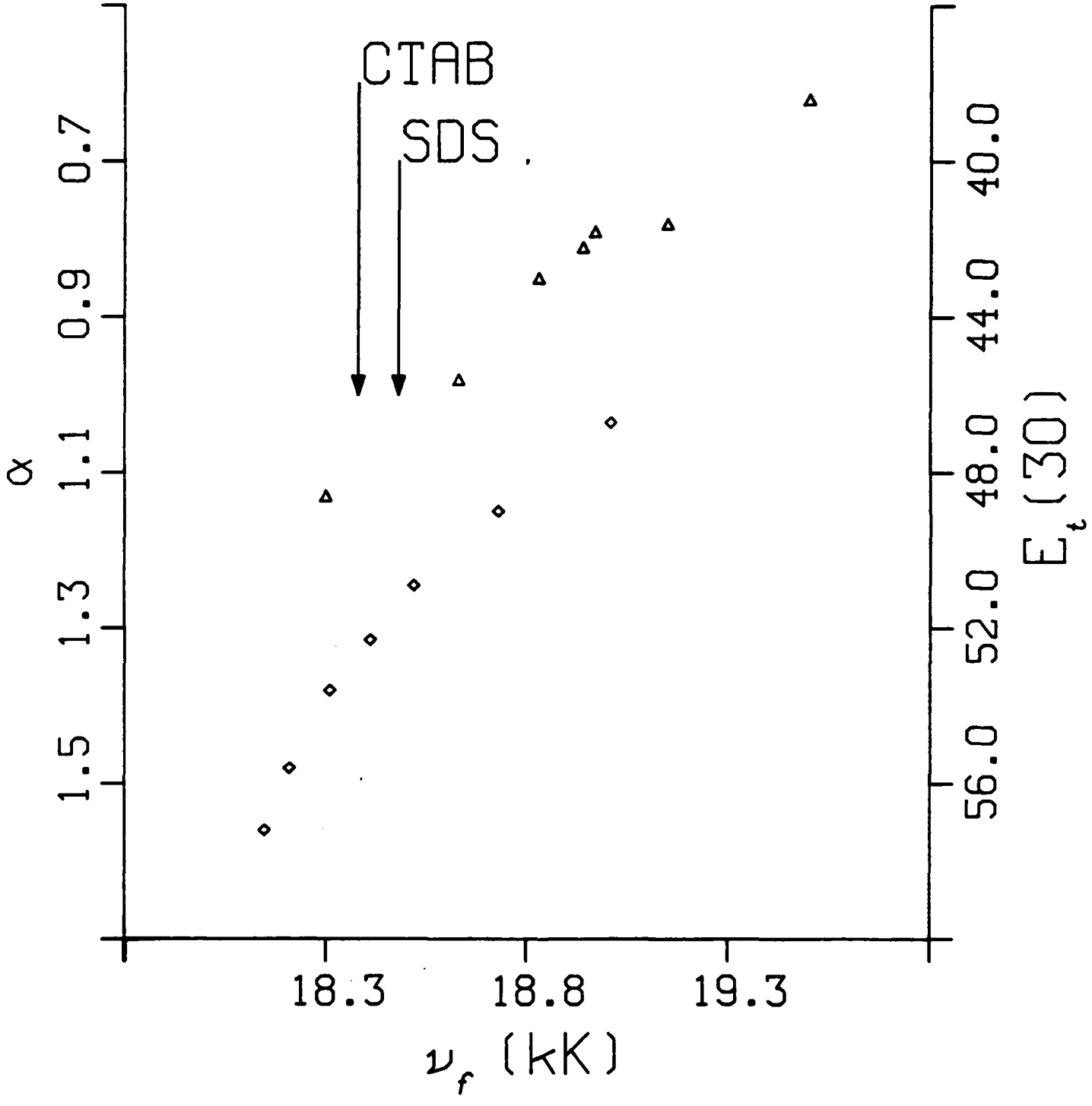
Table 7. Spectral data and fluoresence yields for coumarin dyes in aqueous cyclodextrins[a]

| | $\lambda_a$ (nm) | $\lambda_f$ (nm) | $\phi_f$ |
|---|---|---|---|
| 1 | 380 | 445 | (0.08) |
| 2 | 406 | 505 | (0.009) |
| 4[b] | 427 | 535 | c |

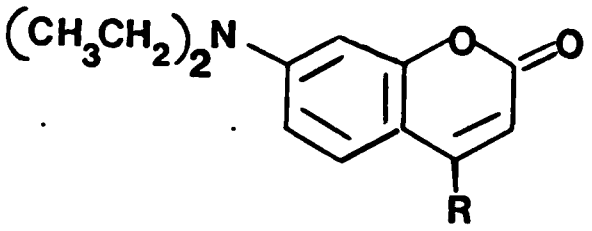
[a] 10 mM β-CD and 0.02 mM dye, except where noted. Solutions were slightly turbid, so that $\phi_f$ values may be only approximate.

[b] 10 mM γ-CD, 0.006 mM dye

[c] not measured but fluorescence weak

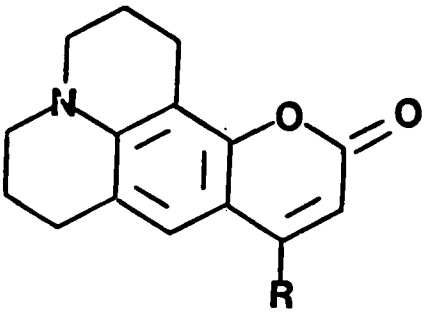

CTAB
SDS
α
0.7
0.9
1.1
1.3
1.5
40.0
44.0
48.0
52.0
56.0
$E_t$ (30)
18.3
18.8
19.3
$\nu_f$ (kK)

Figure



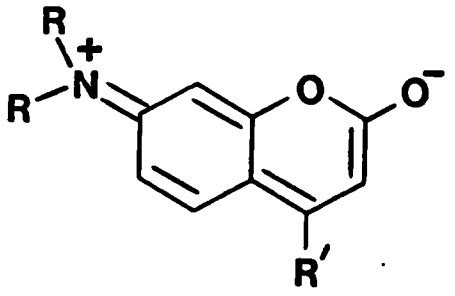
1, R = $CH_3$

2, R = $CF_3$

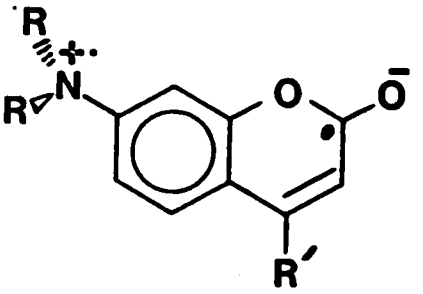


3, R = $CH_3$

4, R = $CF_3$



5



6