Excitation Wavelength Dependence of ACRYLODAN Fluorescence Spectra in Some Polar Solvents

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The fluorescence of ACRYLODAN (6-acryloyl-2-dimethylamino-naphtalene) consists of two bands in liquid polar solvents like 1,2-dichloroethane, N,N-dimethylformamide, or acetonitrile. The intensity ratio of long emission (LE) and short emission (SE) bands, LE/SE, depends on the excitation wavelength. For λ_{exc} = 420 nm only LE band appears. The observed two fluorescence bands of ACRYLODAN in polar solvents containing trace amounts of water originate from two different components: LE of ACRYLODAN and SE of the product resulting from hydrolysis back to 2-dimethylaminonaphtalenic acid.

Key words: Solvatochromic Fluorescence Band Shifts; ACRYLODAN-Fluorescent Probe; Dual Fluorescence.

1. Introduction

PRODAN (6-propionyl-2-dimethylamino-naphtalene), BADAN (6-bromoacetyl-2-dimethylamino-naphtalene) and ACRYLODAN (6-acrylolyl-2-dimethylamino-naphtalene) belong to fluorophores showing special sensitivities to solvent polarity [1]. In particular, ACRYLODAN (Fig. 1) was found to be a very useful fluorescent reagent [2].

While investigating electric dipole moments in the ground, μ_g, and excited state, μ_e, for the above mentioned fluorophores, using the solvatochromic method [3–5], it was found that only ACRYLODAN exhibits two fluorescence bands which are excitation wavenumber-dependent. PRODAN, BADAN, and ACRYLODAN have in position 2 of naphtalene the same substituent $N(CH_3)_2$ which plays a role of an electron donor, whereas in position 6 they have different acceptor substituents. BADAN and PRODAN differ only in the substituents Br and CH_3, respectively, but for ACRYLODAN the acceptor substituent is markedly different. Therefore, for ACRYLODAN much higher values of the dipole moments, μ_g and μ_e, were obtained [5].

The present work reports on the effect of the excitation wavelength on the location and distribution of the fluorescence band intensity for ACRYLODAN in non-polar and polar liquid solvents at 296 K and at 77 K, as well as in rigid PVA solutions at 296 K.

2. Materials and Methods

ACRYLODAN (6-acrylolyl-2-dimethylaminonaphtalene) was purchased from Molecular Probes Europe BV, The Netherlands, and it was used without further purification. The purity of ACRYLODAN is 98%. Isotropic poly(vinyl alcohol) (PVA) films were prepared by the method described in [6]. Absorption and fluorescence spectra were measured by methods described in [7].

3. Results and Discussion

In the case of ACRYLODAN in unpolar solvents, such as *n*-hexane [$f(\varepsilon, n) = 0.0043$]* and cyclohexane [$f(\varepsilon, n) = -0.0065$], for different excitation wavenumbers, $\tilde{\nu}_{\text{exc}}$, only one fluorescence band is observed, and the intensity distribution slightly depends on $\tilde{\nu}_{\text{exc}}$, whereas the location of the fluorescence peaks remains invariant.

In weakly polar solvents like ethyl acetate [$f(\varepsilon, n) = 0.4902$] and 1,2-dichloroethane [$f(\varepsilon, n) = 0.6225$] one

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* $f(\varepsilon, n)$ is the solvent polarity function given by [8]

$$f(\varepsilon, n) = \frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right),$$

where ε is the electric permittivity and n is the refractive index of the solvent.

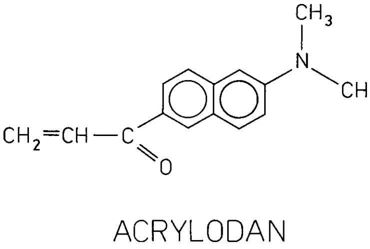

Fig. 1. Structure of ACRYLODAN.

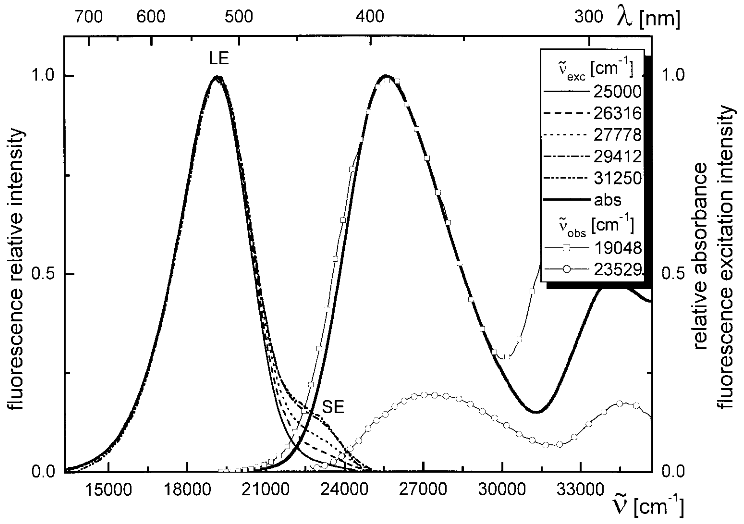

Fig. 2. Fluorescence, absorption and excitation spectra of ACRYLODAN in 1,2-dichloroethane at different excitation wavenumbers $\tilde{\nu}\,[\mathrm{cm}^{-1}]$.

can observe additionally the formation of a fluorescence band at shorter wavelengths (e.g. for greater $\tilde{\nu}$ values) of the spectrum (Fig. 2) for the excitation shifted from 25000 cm^{-1} to 31250 cm^{-1}. Both in ethyl acetate and in 1,2-dichloroethane the intensity distribution and maximum location of the long wavelength emission band (LE) does not depend on $\tilde{\nu}_{\mathrm{exc}}$.

In strongly polar solvents like N,N-dimethylformamide $[f(\varepsilon, n) = 0.8336]$ and acetonitrile $[f(\varepsilon, n) = 0.8636]$ the intensity of the short band (SE) systematically increases with the excitation wavenumber $\tilde{\nu}_{\mathrm{exc}}$ (Figs. 3 and 4). Excitation at increasing $\tilde{\nu}_{\mathrm{exc}}$ does not change the location of the LE band, but it causes only the intensity enhancement in SE with growing solvent polarity function $f(\varepsilon, n)$. For acetonitrile the SE band intensity exceeds that of the LE more than twice at the excitation $\tilde{\nu}_{\mathrm{exc}} = 29412$ cm^{-1} (Fig. 4).

The LE band of ACRYLODAN is extremely strong red-shifted in suitable polar solvents, while the location of the SE band is very weakly dependent on the solvent polarity. In our previous paper [5] the values of μ_{g} and μ_{e} were determined from the shifts of LE bands in solvents with different ε and n by excitation at $\tilde{\nu}_{\mathrm{exc}} = 23810$ cm^{-1} ($\lambda_{\mathrm{exc}} = 420$ nm). In this case only the LE band can be observed.

Similarity between the behaviour of dual fluorescence of ACRYLODAN and that of 4-cyano-N,N-dimethylaniline (CDMA [9–12] can be observed with the difference, however, that the first phenomenon appears as excitation wavelength-dependent whereas the second one does not. Interpretation of CDMA dual fluorescence has been given by Lippert et al. [9, 10] and Grabowski et al. [12]. An essential role in the formation of LE band is played by two different processes: dielectric relaxation of solvent polar molecules around the CDMA molecule or the so called twisted intramolecular charge transfer. In rigid glassy solutions the two mentioned processes do not occur. The results of fluorescence spectra measurements in ethyl acetate and N,N-dimethylformamide at low temperature, $T = 77$ K, are presented in Figs. 5 and 6, respectively. In both cases only one fluorescence band is observed. At the long wavelength part of the spectra at 77 K one can additionally observe the overlapping with the phosphorescence band. Also in a rigid polymer like poly(vinyl alcohol) film (PVA) only one fluorescence band is observed for ACRYLODAN at 296 K. Therefore, similarity exists between the behaviour of ACRYLODAN fluorescence spectra and those of CDMA in rigid environments with rare exceptions like for example CDMA in PVA [13] and polymethylmethacrylate (PMMA) glass [14].

Besides, also the effect of excitation wavelength ($\lambda_{\mathrm{exc}} = 320$ nm and $\lambda_{\mathrm{exc}} = 420$ nm) on the intensity distribution and location of fluorescence bands for low and high ACRYLODAN concentrations in acetonitrile was investigated, and no excimer fluorescence was found.

The fact that only for ACRYLODAN dual fluorescence is observed with increasing the excitation wavenumber $\tilde{\nu}_{\mathrm{exc}}$ from 23810 cm^{-1} to 31250 cm^{-1} compared with PRODAN and BADAN can be explained only by

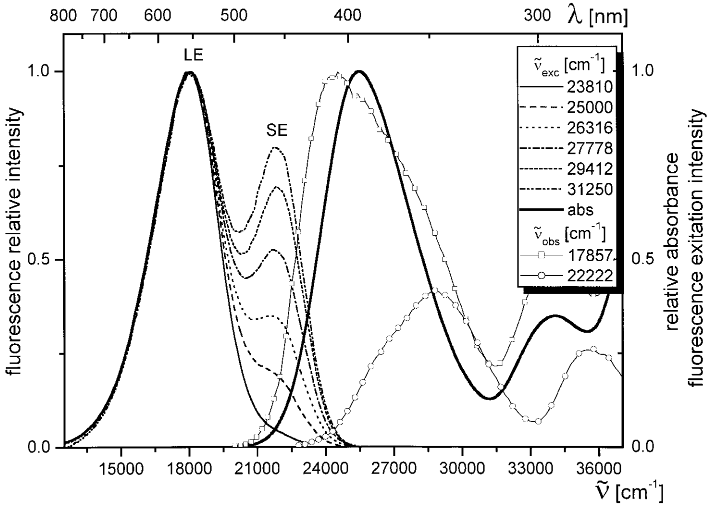

Fig. 3. Fluorescence, absorption and excitation spectra of ACRYLODAN in N,N-dimethylformamide at different excitation wavenumbers $\tilde{\nu}$[cm^{-1}].

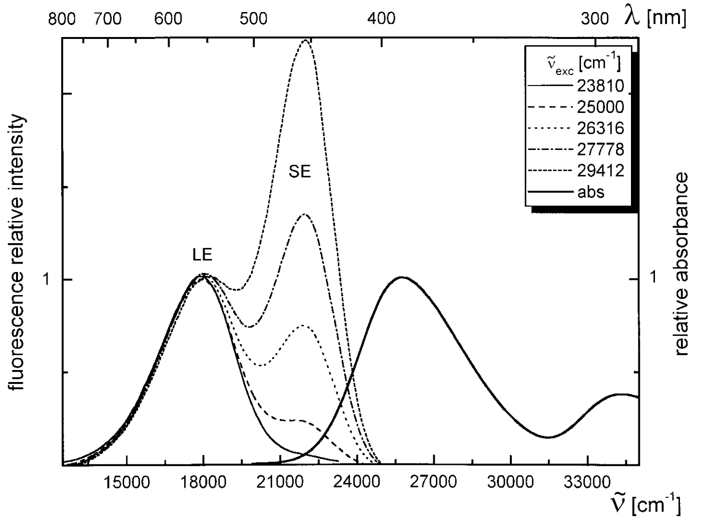

Fig. 4. Fluorescence and absorption spectra of ACRYLODAN in acetonitrile at different excitation wavenumbers $\tilde{\nu}$[cm^{-1}].

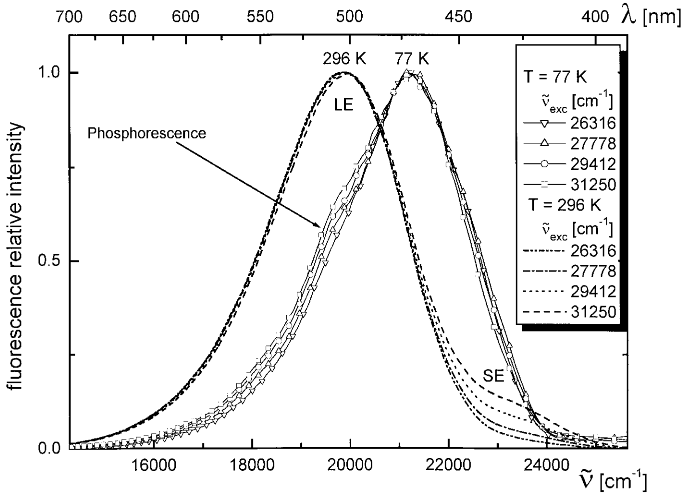

Fig. 5. Fluorescence spectra of ACRYLODAN in ethyl acetate at 296 K and 77 K, measured at different excitation wavenumbers $\tilde{\nu}$[cm^{-1}].

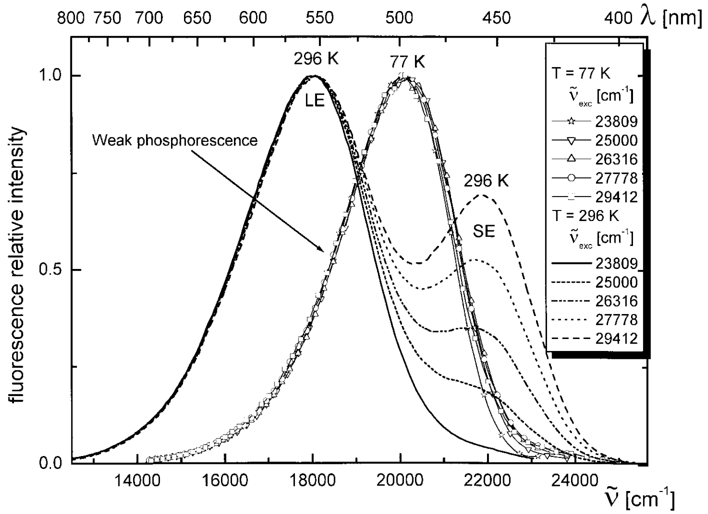

Fig. 6. Fluorescence spectra of ACRYLODAN in N,N-dimethylformamide at 296 K and 77 K, measured at different excitation wavenumbers $\tilde{\nu}$[cm^{-1}].

the presence of two molecular species in the ground state. This fact is strongly supported by the measured fluorescence excitation spectra for ACRYLODAN in the solvents studied. For example, Figs. 2 and 3 show excitation spectra for ACRYLODAN in 1,2-dichloroethane and in N,N-dimethylformamide, respectively.

Pure ACRYLODAN in polar solvents containing traces of water (1,2-dichloroethane, N,N-dimethylformamide, acetonitrile) undergoes a slight degradation as a result of hydrolysis back to 2-dimethylaminenaphtalenic acid. The generated ethene gas evaporates, leaving no other detectable side products.

This fact has been confirmed chromatographically. It was found that the admixture mentioned above is 10% in the case of ACRYLODAN in acetonitrile. Hence, the observed two fluorescence bands of the compound studied in polar solvents originate from two components: LE from ACRYLODAN and SE from the product resulting from hydrolysis. SE is not observed in unpolar solvents like *n*-hexane or cyclohexane which do not contain the traces of water.

4. Conclusion

The observed excitation wavelength effects on both LE and SE bands can be explained in terms of two different kinds of molecules in the ground state, which takes place for solvents containing traces of water.

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