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The influence of ammonia, acetic acid and water vapour on the fluorescence of a 2-naphthol derivative in the Langmuir–Blodget films

AGNIESZKA MIROŃCZYK[1], ANDRZEJ JANKOWSKI[1*], ANTONI CHYLA[2], ANDRZEJ OŻYHAR[3], PIOTR DOBRYSZYCKI[3]

[1]University of Zielona Góra, Institute of Biotechnology and Environmental Science, ul. Monte Cassino 21b, 65-561 Zielona Góra, Poland

[2]Wrocław University of Technology, Institute of Physical and Theoretical Chemistry, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

[3]Wrocław University of Technology, Institute of Organic Chemistry, Biochemistry and Biotechnology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

2-naphtholo-6-sulfonamide (NSDA) undergoes an excited state proton transfer to the environment when incorporated into Langmuir–Blodget (LB) films. We present the effect of acetic and hydrochloric acids, as well as ammonia and water vapour, on the fluorescence and absorption spectra of LB films. Acetic acid inhibits deprotonation of the excited state (ESDP), enormously (by up to 2 orders of magnitude) increases the fluorescence quantum yield (Φ) of NSDA, blue-shifting its fluorescence band. The influence of hydrochloric acid on the fluorescence of NSDA is similar, although the enhancement of Φ is lower in this case. Ammonia leads to the promotion of ESDP and an increase in Φ. Water vapour does not change the fluorescence intensity markedly but it increases the probability of ESDP. These observations can be explained by the formation of a complex between acetic acid and NSDA, and by limited penetration of ammonia and water into the film.

Key words: *2-naphthol; fluorescence; Langmuir–Blodgett films*

1. Introduction

The fluorescence of some dyes and aromatic compounds included into Langmuir –Blodgett (LB) films has been extensively studied [1–6]. Only scarce information is available in the literature, however, on the spectroscopy of compounds in LB films undergoing excited state proton transfer [1, 7]. The fluorescence spectra of such com-

*Corresponding author, e.mail: jjj@wchuwr.chem.uni.wroc.pl.

pounds are very sensitive to the presence of acid and base vapours, due to varying proportions of the protonated (ROH^*) and ionic (RO^{-*}) forms of the fluorophore taking part in deprotonation of the excited state (ESDP) (Fig. 1). Therefore, one may expect that these substances, incorporated in LB films, may find application as chemical sensors [8] and signal processors [9]. On the other hand, investigations of the response of these substances to changes in atmosphere composition may throw a light onto the structure and physicochemical properties of LB films. We have shown [1] that 2-naphtolo-6-sulfonamide of dodecylamine (NSDA) included in a LB film can undergo ESDP to the environment. The scope of the present work is to explore the influence of gases on the electronic spectra of 2-naphthol derivatives in LB films.

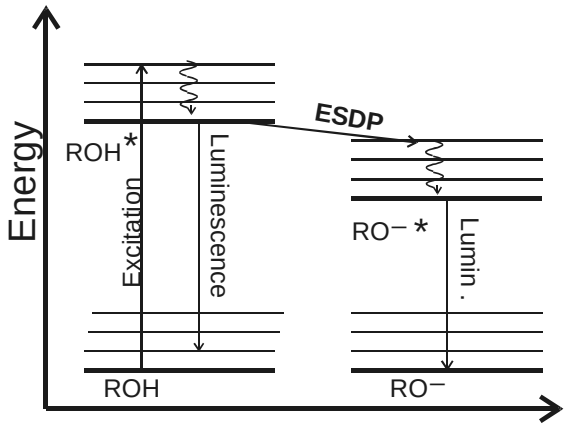

Fig. 1. Energy levels of the system. ROH, RO^- and ROH^*, RO^{-*} designate NSDA molecules in the ground and excited electronic states, respectively. Curled arrows represent radiationless equilibration to the lowest excited state oscillatory level

The results are explained in terms of changes in the film structure under the influence of absorbed gases, penetrating into the layers and creating complexes with NSDA. The influence of modifying of the film composition by adding hydrophobic peptides (gramicidin A) on the film properties has also been studied.

2. Materials and methods

The synthesis of 2-naphtholo-6-sulfonamide of dodecylamine (NSDA), its chemical structure, and absorption, fluorescence, and phosphorescence properties are described elsewhere [1]. Gramicidin A from *Bacillus brevis* was purchased from Fluka and kept in 4 °C.

LB films containing NSDA were deposited onto quartz plates using a KSV-5000 trough (KSV, Finland) by means of a vertical dipping procedure. LB films of pure NSDA, as well as binary systems of NSDA with stearic acid or octadecylamine (0.05–0.2 mol fraction) were used. In some cases, gramicidin (G) was added to the system. The surface tension, transfer ratio, barrier speed, and diving and lifting speed were controlled during deposition. The average area per one molecule estimated for

pure NSDA films was 0,323 nm^2. Transfer isotherms of NSDA and NSDA diluted with stearic acid are shown in Figs. 2 and 3, respectively.

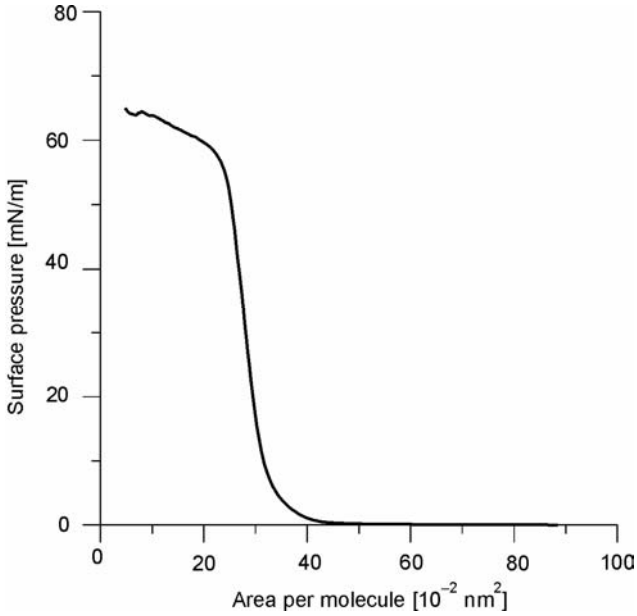

Fig. 2. The transfer isotherm of NSDA

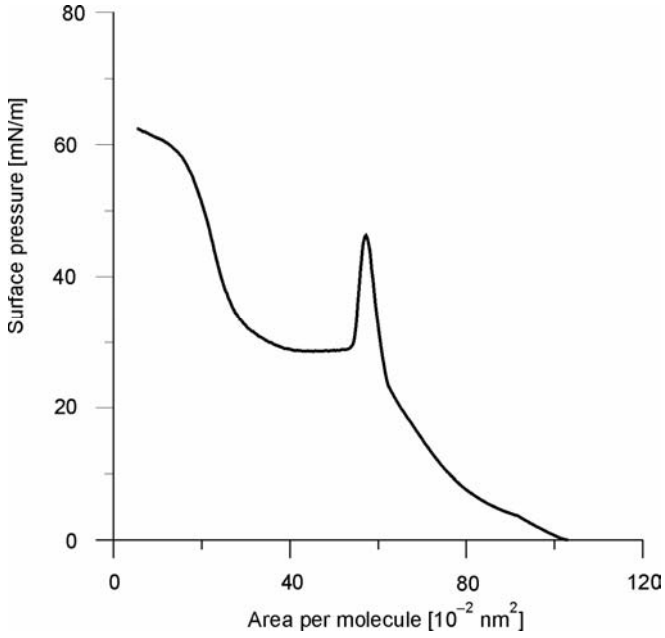

Fig. 3. The transfer isotherm of NSDA (0.1 molar fraction) diluted with stearic acid

To improve the anchoring of NSDA, the substrates (quartz plates) were covered prior to its deposition with a monomolecular layer of stearic or tricosanoic acid, with hydrophilic groups directed to the plate. The remaining procedure of LB film deposition depends on the type of layout required. The head to tail (○— ○—) layout was obtained by upstroke movements of the substrate, initially placed under water. Before consecutive dippings, the films were left to dry and the water surface was cleaned. Repeating this procedure gave the layout required. In most cases, the transfer ratio was close to 1.

3. Results and discussion

3.1. The absorption and fluorescence spectra of NSDA in LB films

Two characteristic bands can be discerned in the absorption spectra of LB films of NSDA at 210 nm (the absorbance of a 3-layer film being 0.073) and 320 nm (absorbance being 0.020). A low noise-to-signal ratio of about 5% and good reproducibility of the spectra confirms fair stability of the structures investigated.

Table 1. Absorption characteristics of NSDA in organic solvents and LB films (3 layers of NSDA)

System	Absorption maxima[a] [nm]		
	Band 1 (L_a)	Band 2 (L_b)	Band 3 (L_b)
NSDA in hexane	288	317	332
NSDA in $CHCl_3$	286	320	337
NSDA in CH_3OH	286	318	335
NSDA in LB film	300	320	337

[a] L_a and L_b are the electronically excited levels of aromatic molecules according to Platt's notation.

The wavelengths of absorption band maxima for NSDA in organic solvents and in LB films are presented in Table 1. The absorbance at 320 nm was used to determine the fluorescence quantum yield.

In the fluorescence spectra of NSDA in LB films, two bands can usually be distinguished, centred at 370–393 nm (LM1) and 430–468 nm (LM2) [1]. The first one may be attributed to the protonated (ROH^*) form of NSDA and the other to its ionic (RO^{-*}) form. The positions of LM1 and LM2, as follows from the band separation procedure [1], depend on the degree of aggregation of NSDA molecules in the LB film. The fluorescence quantum yield Φ, defined as a sum of the band heights at LM1 and LM2, and the excited state lifetime (τ) of selected layers of NSDA in LB films and of the analogous compound 2-naphtholo-6-sufonamide of glycine (2-NSGly) in methanol solution are given in Table 2. Both the fluorescence quantum yields and lifetimes for all LB films are greatly reduced, and that the positions of the absorption and emission bands are red shifted with respect to those of solutions.

Table 2. Fluorescence quantum yields (Φ_n), excited state lifetimes (τ), and ROH* band positions ($LM1_n$) in a neutral atmosphere

Sample Label[a]	Film layout	Φ_n	$LM1_n$ [nm]	LM2 [nm]	τ [ns]
2-NSGly[b]	–	0.18	363	454	4.76
1) TN.a	o— o— T:N	1.9×10^{-3}	370	430	0.16
2) TNN.c	o— o— — o T : N : N	7.5×10^{-4}	393	468	
3) TNN.b	o— o— — o T : N : N	4.3×10^{-3}	384	456	
4) TNN.y	o— — o o— T : N : N	1.9×10^{-3}	400	485	
5) NN.c	o— — o N:N	8.8×10^{-3}	373	433	
6) NNN.1	o— o— — o N : N : N	1.7×10^{-4}	380	440	
7) TNS.1 x = 0.123	o— o— T : N+S	7.4×10^{-3}	391	447	0.268
8) TNS.1w x = 0.100	o— o— T : N+S	1.0×10^{-2}	366	422	
9) TNS.3 x = 0.050	o— o— T : N+S	3.3×10^{-2}	369	423	0.319
10) TNSNS.5 x = 0.120	o— o— — o T:N+S:N+S	3.7×10^{-3}	389	468	0.438
11) TNSNS.z x = 0.050	o— —oo— T:N+S:N+S	1.1×10^{-2}	379	442	0.621

[a] x is the molar fraction of NSDA in the mixture, N – NSDA, T – tricosanoic acid, S – stearic acid.
[b] The data for 2-nphtholo-6-sulfonamide of glycine are taken from Ref. [10]

A similar effect was observed for organic chromophores incorporated into LB films [6]. Exploiting this analogy, the observed effects may be contributed to collective excitations (exciton effects) and energy transfer from fluorescent (F) to nonfluorescent (N) centres in the film [11, 12]. It can be noticed (Table 2) that NSDA films diluted with stearic acid (7–11) have much higher fluorescence quantum yields (Φ) than undiluted ones (1–6). Also, the films with higher molar fractions of NSDA and with chromophores closely located (3, 4) usually have lower values of Φ than others. Octadecylamine as a diluter acts more or less similarly to stearic acid. This may be caused by hindering the aggregation of NSDA in films via dilution with nonfluorescent compounds.

3.2. The impact of acetic acid and HCl vapours on the fluorescence quantum yield, lifetime, and position of the ROH* band maximum (LM1) of undiluted NSDA in LB films

When non-diluted LB films of NSDA are exposed to an atmosphere saturated with acetic acid, the dual fluorescence is converted into a one-band spectrum, centred at about 360 nm (LM1) (Fig. 4). A dramatic increase in the fluorescence quantum yield can also be observed. The values of Φ and LM1 for selected layers are presented in Table 3.

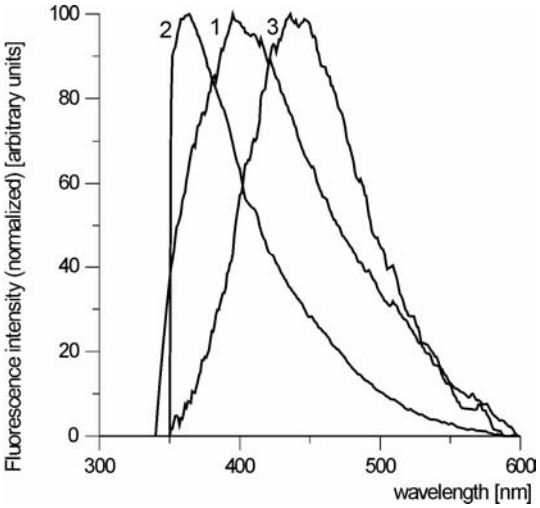

Fig. 4. Fluorescence spectra of the sample T:N:N.c (○— — ○ ○—)
in a neutral atmosphere (1) and under the influence of acetic acid (2) and ammonia (3)

The impact of HCl vapours is similar; the dual fluorescence spectrum is replaced by a one-band spectrum. The effect on the fluorescence quantum yield, however, is much weaker. For instance, the fluorescence quantum yield of sample 4 in Table 3 after adding HCl is 4×10^{-3}.

Table 3. The fluorescence quantum yields (Φ) and positions of ROH* band maxima for samples 1–6[a] in acetic acid (Φ_{AA}, $LM1_{AA}$)

Sample Label[b]	Φ_{AA}	$LM1_{AA}$ [nm]	Δ%[c]
1) TN.a	7.7×10^{-3}	367	75.3
2) TNN.b	1.7×10^{-2}	360	74.7
3) TNN.c	1.9×10^{-3}	375	60.5
4) TNN.y	1.5×10^{-2}	368	87.3
5) NN.c	1.5×10^{-2}	360	41.3
6) NNN.1	3.7×10^{-4}	360	54.0

[a]The samples are labelled in the same way as in Table 2.
[b]Abbreviations are the same as in Table 2.
[c]$\Delta\% = 100(\Phi_{AA} - \Phi_n)/\Phi_{AA}$.

The increase in fluorescence quantum yield in the presence of acetic acid vapour is accompanied by a blue shift of the ROH* band (LM1). Both these spectral changes are accomplished within 10–15 min. These effects in acidic environment are opposite in direction to the changes in Φ and LM1 ascribed to the aggregation process of fluorophore molecules [1]. A possible interpretation is that acetic acid decreases aggregation. This effect may be contributed to the formation of complexes of organic

acid and NSDA [10], which may substantially decrease the interaction between fluorophore molecules. The equilibrium constant of the formation of such complexes cannot not be high, since the fluorescence changes are rapidly reverted (5 min) after removing the acid from the environment.

3.3. The impact of ammonia on the fluorescence quantum yield, lifetime, and position of the RO^{-*} (LM2) band maximum of undiluted NSDA in LB films

The enhancement of the fluorescence quantum yield of the RO^{-*} form of NSDA in ammonia (AM) vapour, estimated with respect to a neutral atmosphere ($\Phi'_{AM} - \Phi'_{n}$) (Table 4) is lower than the analogous change in acetic acid ($\Phi_{AA} - \Phi_{n}$).

Table 4. The fluorescence quantum yields and positions of the RO^{-*} band maxima for samples 1–3[a] in ammonia vapour (Φ_{AM}, $LM2_{AM}$)

Sample Label[b]	Φ_{AM}	$LM2_{AM}$ [nm]	Δ%[c]
1) TN.a	2.0×10^{-3}	430	5.0
2) TNN.b	9.0×10^{-3}	447	52.7
3) TNN.c	1.9×10^{-3}	450	3.8

[a]Sample numbers are the same as in Tables 2, 3.
[b]See comments to Table 3.
[c]$\Delta\% = 100(\Phi_{AM} - \Phi_{n})/\Phi_{AM}$.

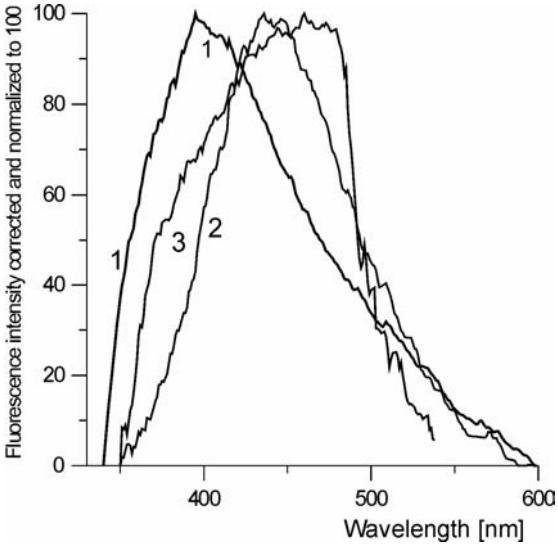

Fig. 5. Fluorescence spectra of the sample TNN.d (○— — ○ ○—)
in a neutral atmosphere (1), in ammonia (2), and after removing NH_3 (3)

The penetration of NH_3 into the film seems to be faster than that of acetic acid, since the changes in the fluorescence spectra are accomplished usually within 1 min after the admission of ammonia, while in acetic acid vapour gradual changes in the fluorescence spectra can be observed for 20 min. Moreover, the changes induced by ammonia are in most cases irreversible after equilibration in ambient atmosphere (Fig. 5), while those in acetic acid are usually reversible under the same conditions. Similarly, the absorption spectra of NSDA in LB films show irreversible changes under NH_3, though the variation is smaller than that of the fluorescence.

One can draw the conclusion that NH_3 interacts with NSDA in the film, but that its penetration is limited to the outer sphere of the fluorophore aggregates, therefore its impact on fluorescence is less marked than that of acetic acid and is achieved faster.

3.4. The influence of acetic acid and ammonia vapour on the fluorescence quantum yield, lifetime, and position of the ROH^* band maximum of NSDA in LB films diluted with nonfluorescent compounds

The increase of the fluorescence quantum yield in acetic acid vapour is higher for pure (undiluted) NSDA films (Table 3) than that for films diluted with stearic acid (Table 5) or octadecylamine. Moreover, the diluted samples, in contrast to undiluted ones, do not show a single emission from ROH^*, but always exhibit dual fluorescence in acetic acid (Fig. 6).

Table 5. The fluorescence quantum yields and positions of the ROH^* and RO^{-*} band maxima for NSDA diluted by nonfluorescent compounds in acetic acid (Φ_{AA}, $LM1_{AA}$) and ammonia vapour (Φ_{AM}, $LM2_{AM}$)

Sample[a]	Φ_{AA}	$LM1_{AA}$[b] [nm]	Φ_{AM}	$LM2_{AM}$ [nm]	Δ%[c]
1) TNS.1	1.7×10^{-2}	387	–	–	56.4
2) TNS.1w	2.5×10^{-2}	360	2.1×10^{-2}	443	60.0
3) TNS.3	1.8×10^{-1}	360	–	–	81.6
4) TNSNS.5	8.7×10^{-3}	381	–	–	57.4
5) TNSNS.z	2.9×10^{-2}	369	–	–	62.0

[a]Sample numbers correspond to No. 7–11 of Table 2, respectively.
[b]Abbreviations the same as in Table 2.
[c]$\Delta\% = 100(\Phi_{AA} - \Phi_n)/\Phi_A$.

The increase of Φ' in AM ($\Phi'_{AM} - \Phi'_n$) is also higher for the undiluted samples than that for the diluted ones. Such results suggest that aliphatic acid or octadecylamine, used for dilution, are included into the molecular aggregates of the fluorophores in the film. In some cases, acetic acid or ammonia can replace long-chain analogues in the aggregates. This would explain a less marked influence of the gases on the spectra compared to the undiluted samples. Similar to undiluted samples, the impact of NH_3 is also irreversible for the diluted ones.

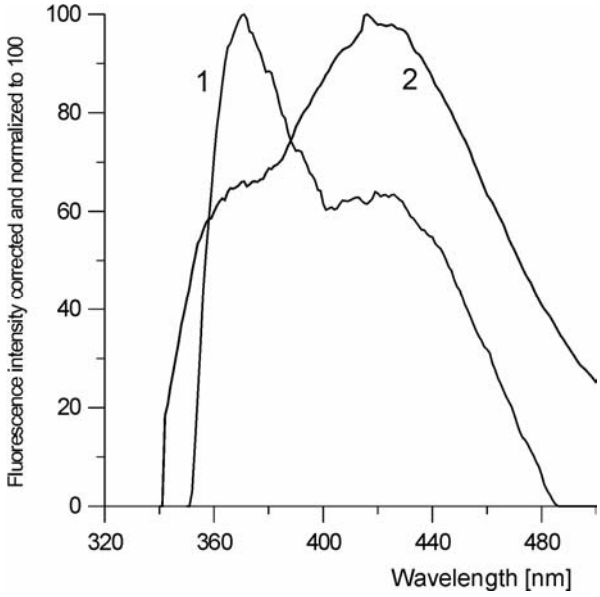

Fig. 6. Fluorescence spectrum of two samples of NSDA diluted with octadecylamine or stearic acid in acetic acid vapour after 30 min: curve 1 – film layout S:N+S, x = 0.098, curve 2 – film layout ○— ○— — ○ S:N+O:N+O, x = 0.098 (S – stearic acid, N – NSDA, O – octadecylamine, x – molar fraction of NSDA)

We have found the ratio Φ_{AA}/Φ_n to be between 2 and 10, and Φ'_{AM}/Φ'_n in most cases between 1 and 2 (Tables 2 and 4). At the same time, the ratios of the lifetimes of the excited states, τ_{AA}/τ_n and τ_{AM}/τ_n, are lower (eg. for sample 11 in Table 2, τ_n = 0.621 ns and τ_{AA}= 0.810 ns). The lack of proportionality between changes in Φ and τ may be explained by various influence of the organic acid on NSDA molecules in the fluorescent (F) and nonfluorescent (N) domains of the film.

3.5. Correlation between the position of the ROH* band maximum (LM1) and fluorescence quantum yield and lifetime

As mentioned above, the reduction of the fluorescence quantum yield of NSDA in LB films with respect to that of the analogous compound in methanol is caused by the aggregation of chromophores and by the excitonic interaction of their electronic transition moments. For the same reason, we observe a spectral shift toward the red. Therefore, the decrease in Φ should correlate with the red shift of the band maxima (LM1 and LM2). The dependence of Φ on LM1 for NSDA diluted with stearic acid is shown in Fig. 7.

The data in Table 3 suggest that the limiting value of the ROH* band position, which should be observed if acetic acid induces complete dissociation of aggregated NSDA molecules, is close to 360 nm.

This fact, together with the correlation of Φ with LM1 (Fig. 7), suggests that at 360 nm the fluorescence quantum yield in the absence of ESDP and exciton effects (Φ_{00}) should be close to 0.04. This value is much lower than that for the analogous compounds in methanol (0.18) [6] which means that, even if NSDA molecules in the fluorescent centres (F) of a LB film do not interact with each other, there must be a certain number of NSDA molecules in the nonfluorescent (N) centres that contribute to the strong reduction of the fluorescence quantum yield. A correlation of the mean lifetime τ of the excited state with LM1 by linear regression (r = 0.86) yields the limiting value, τ_{00}, near 1 ns. Correlations of Φ and τ with LM1 were obtained only for the samples in which NSDA was diluted with stearic acid. For undiluted NSDA in LB films, the correlation is worse.

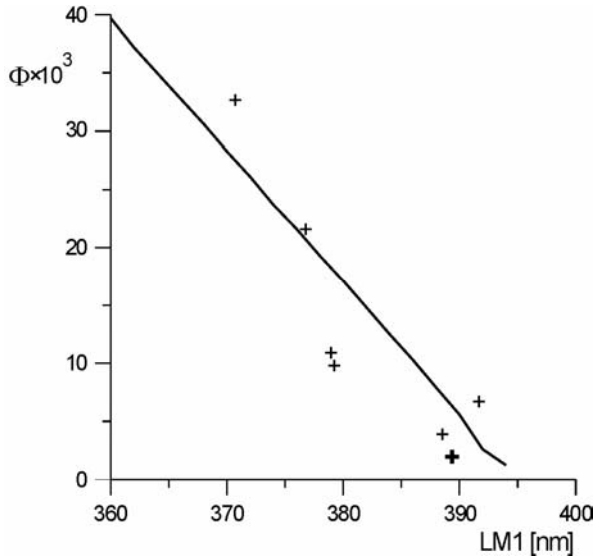

Fig. 7. The correlation of the ROH* band maximum position (LM1) with the fluorescence quantum yield for NSDA diluted with stearic acid. Correlation coefficient r = 0.81

3.6. The influence of water on the fluorescence spectra of NSDA in LB films

It has been found that for NSDA in organic solvents and their mixtures with water the rate and efficiency of ESDP depends critically on the content of water [10]. It may be concluded by analogy to ESDP in solutions, that water molecules penetrating into the layer probably play the role of proton acceptors in LB films.

NSDA films diluted with aliphatic acid or octadecylamine and equilibrated in a laboratory atmosphere (humidity ca. 55%) show slight blue shift after injecting water to bottom of the measuring cuvette. The changes are subtle, but well reproducible for the diluted samples. In contrast to this, the fluorescence spectra of undiluted samples are much more sensitive to water (Fig. 8).

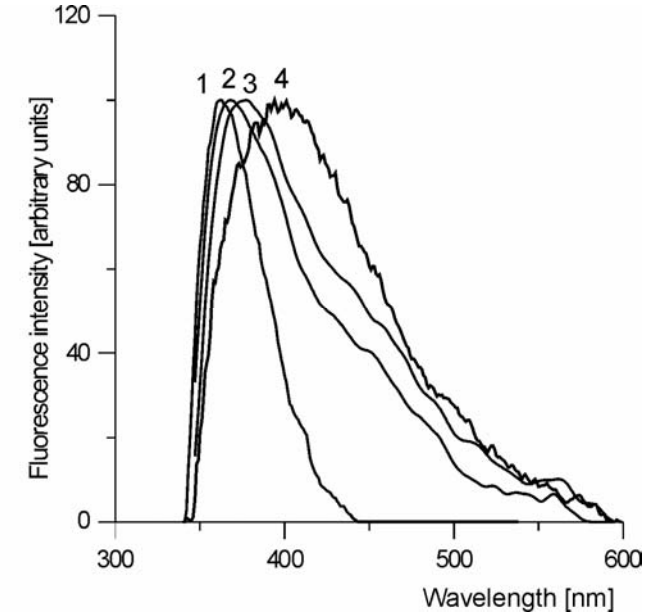

Fig. 8. Changes in the fluorescence spectrum of the sample T:N:N.d (○— ○— — ○) under the influence of water and acetic acid: in acetic acid (1), in H_2O 10 min (2), in H_2O 20 min (3), in a neutral atmosphere (4) (see also Fig. 5 of [1])

The spectrum obtained immediately after drying the sample in a vacuum desiccator differs significantly from the spectrum of the same sample equilibrated at ambient atmosphere (Fig. 5 of ref. [1]). Even the spectrum recorded in a laboratory atmosphere (humidity 55%) is considerably changed by the addition of 0.05 cm^3 of water to the bottom of measuring cuvette. The changes are markedly dependent on time (Fig. 8). After increasing humidity, the fluorescence band is blue-shifted within 10 minutes to almost its position in the spectrum in acetic acid. This effect may be caused by partial dissociation of the aggregates of NSDA in water. After some time (a further 10 min), the emission band is red-shifted, approaching its position in a neutral atmosphere, and the intensity of the other band at about 450 nm, attributed to the RO^{-*} form, increases. This last process may occur as an answer to the increasing rate of ESDP by the formation of hydrogen bonds with water molecules.

3.7. The influence of gramicidin A on the penetration of gases into LB films containing NSDA

Gramicidin (G) is a peptide antibiotic that increases the permeability of cell membranes to protons, thus uncoupling the energy transforming mechanism of the cell. G forms channels in cell membranes, with hydrophobic residues directed outside and hydrophilic CO and NH groups oriented inside the channel and forming intramolecular hydrogen bonds [13].

The effect of G on the permeation of acetic acid into the LB film is depicted in Fig. 9. As stated above (section 3.4), the dilution of NSDA by stearic acid (S) in LB film inhibits the penetration of acetic acid into the specimen, which is concluded from the fact that the acid does not influence the shape of the fluorescence spectrum as it does in undiluted films.

The impact of acetic acid in the case of undiluted samples is contributed (section 3.2) to the formation of complexes with NSDA. If gramicidin A is added to a layer of NSDA, the change in the spectrum is characteristic of undiluted samples and consists of band narrowing and a blue spectral shift after the admission of acetic acid (Fig. 9, curve 4). It follows that G promotes the penetration of acetic acid into films diluted with S. The addition of G to the nonfluorescent layer of S gives no such effect (curve 3). Gramicidin also gives an increase to the permeation of water and ammonia into the film.

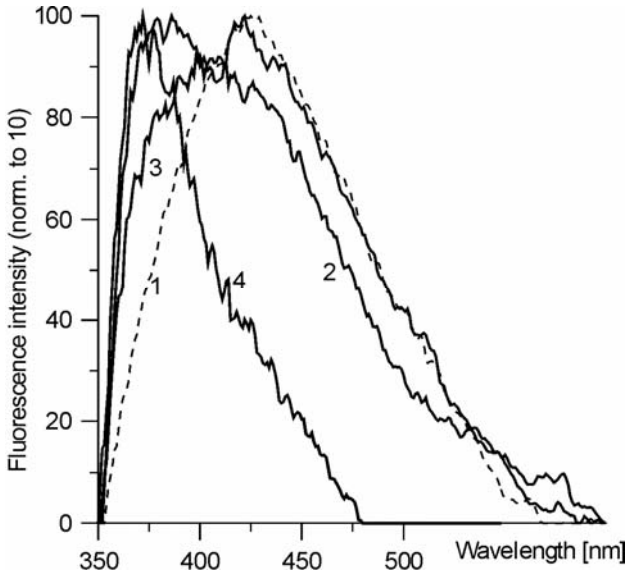

Fig. 9. The influence of gramicidin A on the penetration of acetic acid into LB films. Fluorescence spectra of LB films containing NSDA (N) diluted with stearic acid (S) and gramicidin (G): 1 – in a neutral atmosphere, film layout: ○— — ○ N+S+G: S+G, 2 – sample as in (1) in acetic acid vapour after 2 min, 3 – similar sample with the film layout: ○— — ○ N+S : S+G in acetic acid vapour after 60 min, 4 – sample as in (1) in acetic acid vapour after 20 min

4. Conclusions

The absorption of acetic acid, HCl, NH_3, and water into a LB film strongly affects the fluorescence of NSDA. The observed changes consist in an increase in the fluorescence intensity and a blue shift of the band maximum, probably caused by the intercalation of gas molecules into the layer of NSDA. A small quantity of water is

probably present even in samples dried in a desiccator. Water molecules penetrating the film would approach only the phenolic groups of NSDA, but not the aromatic chromophore. Therefore, increasing the content of water does not greatly influence the structure of NSDA aggregates in LB films. In consequence, the fluorescence quantum yield remains practically unchanged.

Ammonia, on the other hand, promotes excited state deprotonation (ESDP) and enhances, to a limited degree, the quantum yield. It may be therefore assumed that NH_3 also does not interact directly with the fluorophore, but only with water molecules, inducing the polarization of the aggregate as a whole and an irreversible change in the molecular arrangement of the film.

Acetic acid can form complexes with NSDA molecules in LB films, which probably leads to the dissociation of aggregates. The formation of complexes between acetic acid and 2-naphthol analogues has already been postulated for an environment with low polarity (see [10] and references therein). The arising of such complexes can lead to an increase of Φ greater than that in ammonia, due to the dissociation of fluorophore aggregates in the film. Moreover, the binding of acetic acid may also cause the apparent inhibition of ESDP by the rapid reprotonation of the excited phenolate.

The effects described here may be used in molecular switches [9] due to the dependence of the response of samples on atmosphere composition. The possibility of modifying this response by specific additives is another advantageous property of such systems.

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