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A tricyanovinyl azobenzene dye used for the optical detection of amines via a chemical reaction in polymer layers

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Abstract

The reactive tricyanovinyl group of the lipophilic dye 4-*N*,*N*-dioctylamino-4′-tricyanovinylazobenzene dissolved in plasticised PVC interacts with aqueous amines and gives colour changes from blue to orange. Since the conversion of the tricyanovinyl into an 1-amino-2,2-dicyanovinyl group is irreversible, the determination of analyte concentrations has to be performed via kinetic evaluation. The sensitivity of the chemically reactive dye in the polymer layer is highest for lipophilic primary amines and, in the case of aqueous 1-propylamine, covers the range from 0.5 to 4 mM with a limit of detection of 0.1 mM. The maximum signal changes of the chromoreactand in the polymer layer are observed at 642 nm making the probe compatible with cheap light sources and detectors.

Keywords: Tricyanovinyl dyes; Amines; Probe

1. Introduction

In the last two decades azo dyes have found renewed interest due to their possible application in non-linear optical materials [1–4]. Molecules with strong electron donor and acceptor moieties can be synthesized by facile diazotation procedures, thus giving rise to high molecular susceptibilities. Among the azo dyes presented for non-linear optics, azo dyes with tricyanovinyl groups have been presented because of their impressive acceptor strength which is significantly higher than in the case of nitro groups [5,6]. However, it is known that tricyanovinyl groups are susceptible to nucleophilic attack [7,8] which makes these dyes possible candidates for application in optical sensors or as optical probes.

Amines are relevant analytes in food industry because they are released during the degradation of fish and meat and they are found as effluents in agricultural and industrial areas. So far, probes and indicators for amines have been reported that are based on the quenching of fluorescent dyes attached to cyclodextrines [9,10]. Selective fluorescence quenching of polycyclic aromatic hydrocarbons by aliphatic amines has also been investigated [11]. Chromoreactands for amines based on trifluoroacetyl dyes gave reversible colour changes from red to yellow upon interaction with dissolved aliphatic amines [12]. A lithium-complexed calixarene immobilised onto filter paper was found to undergo colour changes from yellow to red in the presence of gaseous trimethylamine

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with a sensitivity in the ppb concentration range [13].

In the present paper the interaction of a tricyanovinyl azobenzene dye dissolved in thin layers of plasticised PVC upon exposure to aqueous aliphatic amines has been investigated and the mechanism of interaction in the membrane was discussed.

2. Experimental

2.1. Reagents and apparatus

For membrane preparation, poly (vinyl chloride) (PVC, high molecular weight), 2-nitrophenyloctyl ether (NPOE) and tetrahydrofuran (THF) were obtained from Fluka. All amines were of analytic reagent grade (Sigma, Fluka). Amine solutions were prepared by dissolving the appropriate amount of each amine in 0.1 M sodium hydroxide solution. Due to the high pH of 13.0, the amines were present in the electrically neutral form and not in the ammonium form. The correct amine concentrations were calculated by using the Henderson–Hasselbach equation and the pK_a value of each amine [14]. The absorbance spectra of the dissolved dye and of amine-sensitive layers were recorded on a Lambda 16 UV–VIS spectrometer (Perkin-Elmer) at 22±1 °C. The polymer layer was fixed in a home-made flow-through cell [15]. The measurements were performed by placing the flow-cell in the spectrometer and pumping the sample solutions through the cell at a flow rate of 1.5 ml min^{-1} using a peristaltic pump. A change in flow from 0.7 up to 3.0 ml min^{-1} did not affect the response behaviour.

2.2. Synthesis of 4-N,N-dioctylamino-4′-tricyanovinylazobenzene (**CR-593**)

Chromoreactand **CR-593** was synthesised according to standard diazotation procedures [5–7]. Tricyanovinylaniline [5] was diazo-coupled to *N,N*-dioctylaniline [16] in acetic acid at 10 °C for 3 h. The resulting lipophilic tricyanovinyl dye **CR-593** was precipitated by addition of aqueous sodium acetate, extracted into dichloromethane and dried over magnesium sulfate. The azo dye was then purified on silica gel using dichloromethane/hexane = (2:1) as the eluent. ^{1}H-NMR (250 MHz, $CDCl_3$) of 4-*N*,*N*-dioctylamino-4′-tricyanovinylazobenzene (**CR-593**), δ (ppm): 8.16 (d, 2H), 7.92 (m, 4H), 6.71 (d, 2H), 3.40 (t, 4H), 1.67 (m, 4H), 1.34 (m, 20H), 0.88 (t, 6H). Calculated for $C_{33}H_{42}N_6$ (522.74): C, 75.82; H, 8.10; N, 16.08, found C, 76.08; H, 8.22; N, 15.82. M.p. 81–83 °C, λ_{max} (acetonitrile) = 593 nm, $\epsilon_{593} = 32\,300$ M^{-1} cm^{-1}, λ_{max} (toluene) = 595 nm, $\epsilon_{595} = 38\,400$ M^{-1} cm^{-1}.

2.3. Membrane preparation

Of the chromoreactand **CR-593**, 1.0 mg was dissolved together with 60 mg of the plasticizer 2-nitrophenyloctyl ether and 60 mg of poly(vinyl chloride) in 0.75 ml of tetrahydrofuran and 0.2 ml of the solution spin-coated on a rotating glass plate (serving as a mechanical support for the polymer layer). The resulting sensor layer **M1** with a thickness of 3–5 µm was placed in ambient air for drying. Membrane **M2** for IR measurements was obtained by dissolving 1.0 mg of **CR-593**, 2.0 mg of PVC and 4.0 mg of NPOE in 100 µl of THF and pipetting 50 µl of the solution on a KBr support resulting in a layer with a diameter of 1 cm.

3. Results and discussion

3.1. Spectral properties of **CR-593** in acetonitrile

Azobenzene dyes with tricyanovinyl groups as acceptors and dialkylamino groups as donors are among the longest wavelength absorbing monoazo dyes. The tricyanovinyl group exhibits a Hammett substituent constant σ_p of 0.98 which is significantly higher than in the case of the nitro group (σ_p of 0.78) [17]. Consequently, the present dye exhibits an absorbance maximum in toluene at 595 nm while the maximum in acetonitrile is found at 593 nm. When the dye in polar acetonitrile is reacted with increasing concentrations of 1-propylamine, then the absorbance maximum at around 593 nm decreases and simultaneously, a new maximum is formed at 459 nm (Figs. 1 and

2). This colour change is caused by the nucleophilic approach of 1-propylamine to the tricyanovinyl group which is then converted into a 1-propylamino-2,2-dicyanovinyl group [8]. The spectral changes upon exposure to 1-propylamine are shown in Fig. 2 and indicate that full conversion takes place at equimolar concentrations. The dye responds to dissolved amines in a ppm concentration range, but the reaction rate is very slow and the chemical reaction is terminated only after several days. A 10-fold increase in amine concentration, however, gives full colour changes within 15–30 min and thus allows to qualitatively assess the presence of amines in organic solvents. The significant changes in absorbance, especially at wavelengths where cheap light sources and detectors are available, allowed to investigate the interaction of the dye with amines in polymer layers.

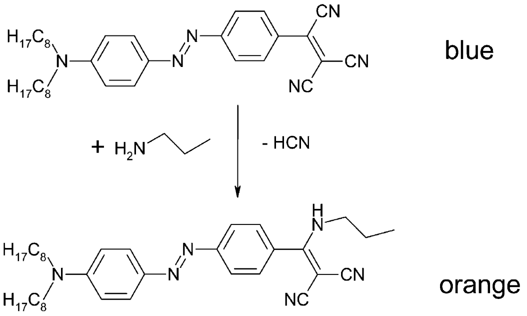

Fig. 1. Chemical reaction of chromoreactand **CR-593** with 1-propylamine in acetonitrile and thin layers of plasticised PVC.

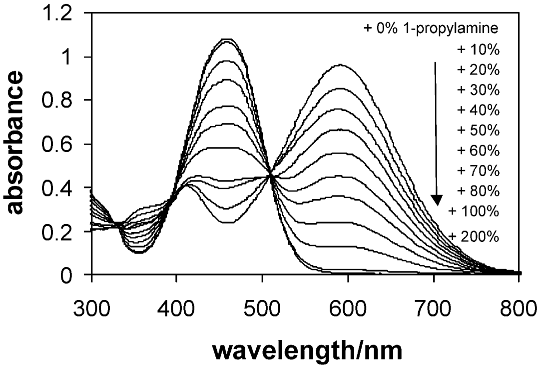

Fig. 2. Change in absorbance of a 27.5 μM solution of chromoreactand **CR-593** in acetonitrile upon exposure to increasing concentrations of 1-propylamine. Concentrations of 1-propylamine are given relative to **CR-593**.

3.2. Response of sensor layers based on ***CR-593*** *toward amines*

The absorbance maximum of **CR-593** in PVC plasticised by 2-nitrophenyloctyl ether (membrane **M1**) is located at 642 nm. Although this is at significantly longer wavelengths than for both toluene and acetonitrile as the solvents, such a strong red-shift has already been observed for other azobenzene dyes as well [16]. Fig. 3 shows the corresponding absorbance spectra upon exposure to 1-propylamine which indicate that only one type of chemical reactions is taking place within the sensor layer due to the presence of clear isosbestic points. Interaction with aqueous 1-propylamine causes the long-wavelength absorbance to decrease linearly because the interaction of the dye with amines is irreversible. Consequently, no steady state signals are observed upon exposure to different concentrations of amines but rather different slopes in absorbance changes versus time. Fig. 4 shows the decrease in absorbance at 630 nm upon exposure to 1-propylamine which is linear at concentrations up to 4.0 mM of 1-propylamine while the response is less linear at higher concentrations. Nevertheless, an evaluation of the

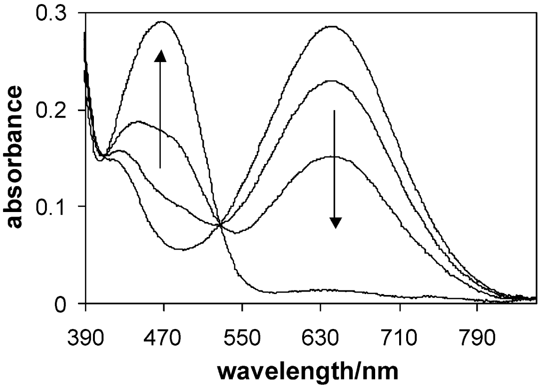

Fig. 3. Change in absorbance of chromoreactand **CR-593** in layer **M1** upon exposure to aqueous 1-propylamine. Due to the irreversible reaction, no steady-state signal can be observed. However, several spectra are depicted to show the isosbestic points which indicate that a single chemical reaction takes place within the polymer layer.

analyte concentration can be performed via the slope of the change in absorbance up to 4 mM 1-propylamine. The sensor layer **M1** exhibits a detection limit of 0.1 mM. The relative standard deviations for the slopes at 0.6 and 2.4 mM 1-propylamine ($n = 3$) for different layers were determined to be as high as 7.5 and 5.6%, respectively, which is due to the limited reproducibility of the layer preparation with our laboratory facilities. The shelf life of the membranes exceeds 6 months.

The selectivity to different amines is represented as different slopes in the absorbance changes. Thus comparable slopes (and selectivity) are observed for 1-butylamine and amphetamine while the response to less lipophilic 1-propylamine, ethylamine and diethylamine is smaller (Fig. 5). Surprisingly, a response, albeit very small, is observed for triethylamine which should not be capable of interacting with the tricyanovinyl group of **CR-593** according to Refs. [7,8]. This suggests a slow hydrolysis of the dye through chemical reaction with hydroxide ion formed from the interaction of triethylamine with water in the membrane. Slow hydrolysis via hydroxide is also confirmed when using polymer matrices with enhanced permeability for hydroxide such as poly(ethylene vinyl acetate) copolymer. When dissolving **CR-593** in such a copolymer and exposing the resulting layer to an aqueous sample of pH 13.0 even without the presence of amines, a slow decrease in absorbance at 630 nm is observed. However, in the present investigation, a combination of PVC and NPOE has been used as the matrix for the dye because this plasticised polymer is virtually impermeable for hydroxide ions, especially when no anion exchange catalyst or anion carrier is present [18].

In order to further investigate the interaction of the chromoreactand with amines in plasticised PVC, sensor layers with enhanced amount of **CR-593** (**M2**) have been prepared and investigated via FT-IR spectroscopy on KBr substrates. The layers showed that the interaction of gaseous 1-propylamine with **CR-593** caused the formation of a broad amino valence vibration at 3334 cm^{-1} with a shoulder at 3270 cm^{-1}. Simultaneously, the nitrile valence vibrations of **CR-593** at 2231 cm^{-1} with a shoulder at 2223 cm^{-1} were shifted to a single band at 2211 cm^{-1} (Fig. 6). A small peak at 2121 cm^{-1} appearing only shortly after exposure to 1-propylamine and later disappearing may be due to gaseous HCN formed during the chemical reaction which slowly evaporated. A similar behaviour in terms of the shift of the nitrile vibrations was observed for gaseous diethylamine, but now the peak at 2211 cm^{-1} also exhibited a shoulder at 2196 cm^{-1} and no valence vibration of

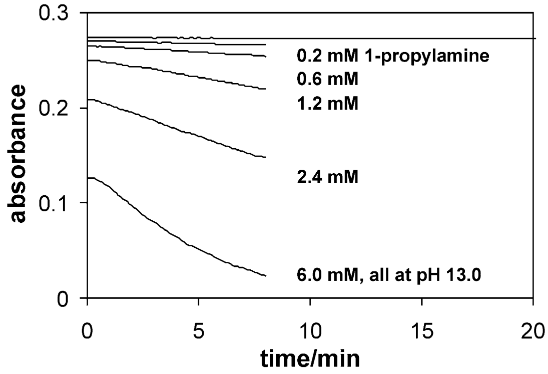

Fig. 4. Response of the sensor layer **M1** based on chromoreactand **CR-593** to different concentrations of aqueous 1-propylamine measured in a flow cell at 630 nm.

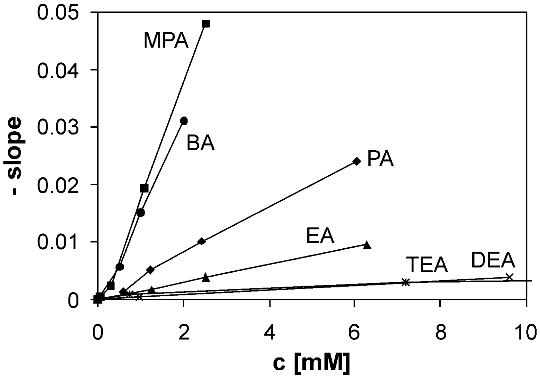

Fig. 5. Calibration points of the sensor layer **M1** upon exposure to different aqueous amines measured at 630 nm. The different slopes of the absorbance changes versus time upon exposure to the analyte were plotted against the analyte concentration; EA, ethylamine; PA, 1-propylamine; BA, 1-butylamine; DEA, diethylamine; TEA triethylamine; MPA, amphetamine.

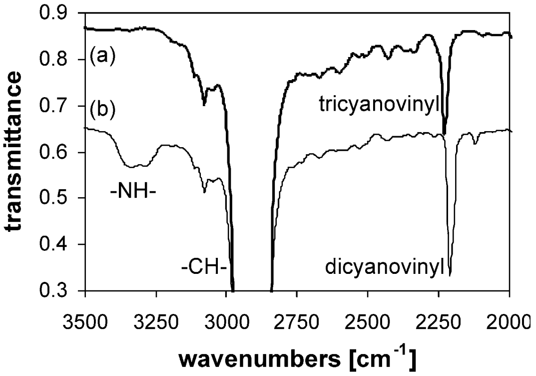

Fig. 6. Layer **M2** (14.3% CR-593, 28.6% PVC, 57.1% NPOE) before (a) and after (b) 10 s exposure to headspace concentrations of gaseous 1-propylamine. The formation of an amino valence vibration and the shift of the nitrile vibration are shown.

an amino group was observed. In the case of gaseous triethylamine, the nitrile valence vibrations of **CR-593** at 2231 cm^{-1} with a shoulder at 2223 cm^{-1} decreased by about 40% and a single peak at 2190 cm^{-1} was formed.

4. Conclusions

A simple probe layer for the detection of lipophilic amines is presented which shows distinct colour changes from blue to orange. Apart from the compatibility to cheap light sources, the advantage of such as probe is that it may be used as a test strip in cuvettes to quantify amine concentrations or to use layers as qualitative indicators for the presence of gaseous amines in air. Another possible application of the dye is the use in a flow injection system with the dye dissolved in appropriate organic solvents. The spectral differences of the IR signal changes allow to obtain additional selectivity in the evaluation of the sensor layers and the polymer layers therefore may also be used in ATR-FTIR devices.

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