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Selective interaction in solution between ammonium groups of a cationic starch and aromatic probes revealed by fluorescence emission

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Abstract

Two fluorescent sensors A1 and A2, designed to complex selectively ammonium groups of cationic starch were synthesized and their fluorescence properties evaluated. They display fluorescence intensity enhancement (FIE) due to the complexation of ammonium group by the 1,2-diazacrown-6 moiety and the side arm of the molecule that limits the electron donor–acceptor interaction between the amine and the anthracene part. The location of the benzene ring in the middle of the side arm in A2 provides better performance for this compound. The FIE presented by A1 and A2 is found quite selective for ammonium compared to sodium, potassium and calcium cations but the response is not linearly related to the ammonium concentration. Also, the FIE is found considerably reduced in water solution. This behavior precludes an easy quantitative application. By contrast, the commercial fluorescent whitening agent (FWA) in water solution displays a quantitative and selective fluorescent response versus the ammonium concentration of cationic starch. This might allows an easy and sensitive way to estimate the amount of ammonium groups (range 10^{-6}–10^{-5} mol l^{-1}) presented by a cationic starch in water solution.

Keywords: Fluorescent sensors; Fluorescent whitening agent; Cationic starch

1. Introduction

The use of additives in the wet part of a paper machine to improve the mechanical strength of the paper web is widely developed in the paper industry [1]. Among them, starch and cationic starch, e.g. starch bearing positively charged ammonium groups as pendant units, are currently used [2–4]. The amount of starch might be measured by NMR spectroscopy in $NaOD/D_2O$ solution [5]. This method allows a complete measurement of the underivatized and derivatized starch concentration but it lacks in sensitivity. The amount of starch in papers might be determined by enzymatic hydrolysis of the starch followed by determination of the glucose liberated by a glucose sensor [5]. A more traditional way consists in the use either of the sulfuric acid/phenol method or the iodine method [6]. The latter is based on the measurement of the absorbance at 578 nm of the complex between iodine and the amylose fraction of the starch. The concentration of cationic starch solution might be evaluated by measuring the electrical charge neutralization by a polyvinyl alcohol sulfate solution revealed by conductimetry (PCD) or by a colored indicator, such as toluidine blue [7]. It was published by Marhold et al. [8] a sensitive fluorimetric assay for surfactant with ammonium group based on the quenching of the fluorescence of 8-octadecyloxypyrene-1,3,6-trisulfonate.

The present communication describes an attempt to determine the concentration of cationic starch in dilute solutions by fluorescence emission either using the probes A1 and A2 specially designed and synthesized for that purpose or using a commercial fluorescent whitening agent (FWA) which presents an emission dependent on the presence of quaternary ammoniums.

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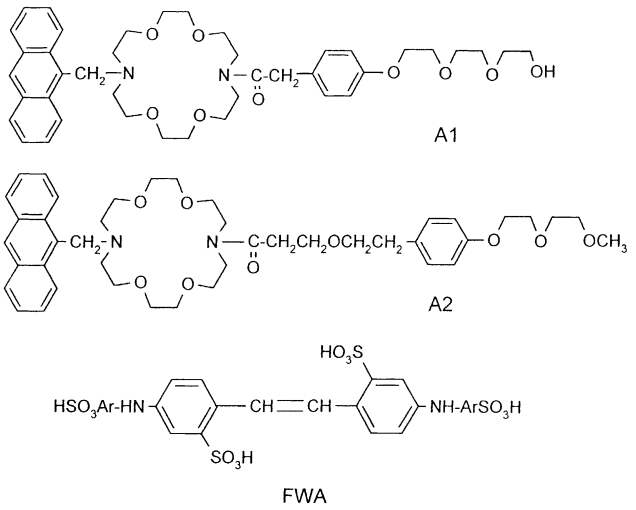


2. Experimental

2.1. General

NMR spectra are recorded on a Bruker AC 250 (reference Me_4Si, solvent $CDCl_3$). The IR and UV absorption spectra are respectively performed on Perkin–Elmer Paragon 1000PC and on Hitachi U-3300 spectrometers. Mass spectra are obtained using a VG Micromass Autospec Q instrument. The fluorescence spectra are recorded on Hitachi F4500 fluorimeter with no correction for the emission. The solutions for fluorescence measurements were undegassed. The synthesized compounds are purified by column chromatography on silica gel (63–200 μm) or neutral alumina (50–150 μm) from Fluka using the appropriate eluents. The purity of the compounds is checked by TLC (silica gel or neutral alumina). The chemicals were obtained mainly from Aldrich and were used without further purification. For spectrometric measurements, it is checked that methanol (spectrometric grade) and distilled water do not present fluorescent impurities. The FWA Blankophor PC, bearing 4 sulfonate groups is a Bayer product manufactured in concentrated solution and kindly given by Smurfit Worldwide Research Europe (Talence, France). The cationic starch Hi-Cat 180 is a commercial modified potato starch from Roquette (France) which is conditioned at 85.3% dryness. The nitrogen content of the starch is equal to 0.65%. Water solutions of the cationic starch Hi-Cat 180 (1 wt.%) at pH = 6 are used for the study with A1 and A2 and at pH = 4.5 for the study with FWA.

2.2. Synthesis of the probes

2.2.1. Probe A1

1-Tosyl-1,4,7,10-tetraoxaundecane is prepared by action for 8 h at 0°C of tosyl chloride (0.25 mol) on triethyleneglycol monomethyl ether (0.25 mol) in pyridine (125 ml). Then dichloromethane (250 ml) is added to dissolve the polyethyleneglycol tosylate and the organic phase is washed with hydrochloric acid (5%), to remove the pyridine. After drying, the organic phase over sodium sulfate and evaporation under vacuum, the tosylate is obtained as a pale yellow liquid (yield 69%). IR (NaCl film), ν, 2880; 1595; 1490; 1450; 1355; 1290; 1175; 1100; 1035; 1010; 925; 820; 775; 680; 665 cm^{-1}. ^1H NMR ($CDCl_3$) δ, 2 ppm (s, 3H); 2.85–3.40 ppm (m, 15H); 3.90–7.40 ppm (m, 4H).

1-Iodo-3,6,9-trioxadecane is prepared by action of NaI (69 mmol) on 1-tosyl-1,4,7,10-tetraoxaundecane (63 mmol) in acetonitrile (200 ml) at 100°C for 18 h. Dichloromethane (100 ml) is added and the organic phase is treated with a solution of $Na_2S_2O_3$ (5%) and washed with water. After drying the organic phase over sodium sulfate and evaporation under vacuum, the iodo derivative is obtained as a yellow liquid (yield 62%). IR (NaCl film), ν, 2875;1455; 1350; 1265; 1200; 1110; 1030; 850; 665 cm^{-1}. ^1H NMR ($CDCl_3$) δ, 3.10 ppm (t, 2H); 3.22 ppm (s, 3H); 3.30–3.50 ppm (m, 8H); 3.60 ppm (t, 2H).

Methyl 4-(1′,4′,7′,10′-tetraoxaundecyl)phenyl acetate is prepared by reaction of methyl (4-hydroxyphenyl) acetate (15 mmol) with 1-iodo-3,6,9-trioxadecane (15 mmol) and K_2CO_3 (116 mmol) in acetonitrile (100 ml) at 100°C for 20 h under magnetic stirring. Dichloromethane (100 ml) is added and the organic phase is treated with a solution of NaOH (10%) and washed with water. After drying the organic phase over sodium sulfate and evaporation under vacuum, the acetate is obtained as a yellow liquid (yield 94%). IR (NaCl film), ν, 2930; 2875; 1735; 1615; 1515; 1455; 1435; 1350; 1245; 1140; 1110; 1065; 1015; 945; 820 cm^{-1}. ^1H NMR ($CDCl_3$) δ, 3.25 ppm (s, 3H); 3.40–3.70 ppm (m, 13H); 3.72 ppm (t, 2H); 3.99 ppm (t, 2H); 6.70–7.20 ppm (m, 4H).

4-(1′,4′,7′,10′-Tetraoxaundecyl)phenyl acetic acid is synthesized by reaction of methyl 4-(1′,4′,7′,10′-tetraoxaundecyl)phenyl acetate (12.5 mmol) with NaOH (15 mmol) in methanol (100 ml)/water (100 ml) mixture at reflux for 1 h. The mixture is acidified to pH 1 with hydrochloric acid (35%) and extracted with diethyl ether. Usual workup and chromatography of the organic residue on silica gel (eluent: Et_2O/CH_3OH (1v/1v) give the acid as a pale yellow liquid (yield 80%). IR (NaCl film), ν, 3550–2500 cm^{-1} (broad band); 1730; 1615; 1510; 1455; 1250; 1130; 1110; 945; 820; 735 cm^{-1}. ^1H NMR ($CDCl_3$) δ, 3.50 ppm (s, 3H); 3.60–4.50 ppm (m, 14H); 6.70–7.40 ppm (m, 4H); 9.3 ppm (s, 1H).

4-(1′,4′,7′,10′-Tetraoxaundecyl)phenyl acetyl chloride is prepared by treating 4-(1′,4′,7′,10′-tetraoxaundecyl)phenyl acetic acid (1.1 mmol) with oxalyl chloride (10 mmol) in benzene (30 ml) at reflux for 5 h under magnetic stirring. The organic solvents are evaporated under vacuum giving the acid chloride as an orange liquid (yield 100%).

N-benzyloxycarbonyl-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane is synthesized following a procedure described by Lehn et al. [9] by addition (5 h) of benzylchloroformate (9.1 mmol) to a solution of 1,10-diazacrown-6 (9.5 mmol) and Et_3N (28 mmol) in benzene (300 ml) at room temperature under magnetic stirring. Then the mixture is treated

three times with 50 ml of water and five times with 100 ml of hydrochloric acid (10%). The aqueous phase is separated from the organic one and made alkaline (pH = 11) by sodium hydroxide (50%). The amine is obtained by extraction with chloroform and evaporation of the solvent (yield 21%). ^{1}H NMR ($CDCl_3$) δ, 2.8 ppm (t, 4H); 3.50 ppm (m, 20H); 4.60 ppm (s, 1H); 5.10 ppm (s, 2H); 7.20 ppm (s, 5H).

N′-((1′,4′, 7′,10′-tetraoxaundecyl)benzylcarbonyl)- *N*-benzyloxycarbonyl-1,10-diaza-4,7,13,16- tetraoxacyclooctadecane is prepared by reacting, at room temperature, *N*-benzyloxycarbonyl-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.65 mol) and 4-(1′,4′,7′,10′-tetraoxaundecyl) phenyl acetyl chloride (1.1 mmol) in triethylamine (7.5 mmol) and benzene (70 ml) for 18 h under stirring. The mixture is treated with sodium hydroxide (10%, 20 ml) for 15 mn and extracted with diethyl ether (100 ml). The organic phase is successively treated with NaOH (10%, 30 ml), HCl (10%, 20 ml) three times and washed with water. Evaporation of the solvent gives the expected compound as a pale yellow liquid (yield 93%). IR (NaCl film), ν, 2925; 2870; 1700; 1640; 1510; 1455; 1415; 1350; 1245; 1115; 685 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ, 3.3 ppm (s, 3H); 3.40–4.0 ppm (m, 38H); 5.1 ppm (s, 2H); 6.9–7.5 ppm (m, 9H).

N′-(1′,4′,7′,10′-tetraoxadecyl)benzylcarbonyl-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane is obtained by reacting the preceding compound (0.6 mmol) with HBr in acetic acid (33%, 10 ml) at room temperature for 4 h. Water (50 ml) and chloroform (150 ml) are added to the reacting mixture. It is made alkaline with NaOH (10%) and extracted with chloroform. The organic phase is dried over sodium sulfate and evaporated under vacuum giving the amine as a pale yellow liquid (yield 60%). ^{1}H NMR ($CDCl_3$) δ, 2.0 ppm (s, 1H); 2.8 ppm (m, 4H); 3.4–3.8 ppm (m, 31H); 3.8 ppm (m, 2H); 4.10 ppm (m, 2H); 6.6–7.2 ppm (m, 4H).

N′-((1′,4′,7′,10′-tetraoxadecyl)benzylcarbonyl)-*N*-(9-anthrylmethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane: A1. 9-Chloromethylanthracene (0.37 mmol), the preceding amine (0.36 mmol), K_2CO_3 (1.4 mmol) in acetonitrile (10 ml) are refluxed for 20 h. Dichloromethane is added to the mixture which is washed with water. Evaporation of the organic phase and chromatography over neutral alumina (eluent CH_2Cl_2/EtOH 99v/1v) gives the compound A1 as a deep-yellow oily product (yield 70%). IR (NaCl film), ν, 2925; 2860; 1730; 1635; 1510; 1455; 1350; 1285; 1245; 1120; 790; 665 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ, 2.80 ppm (m, NCH_2, 4H); 3.30–3.70 ppm (m, OH + OCH_2 + C_6HCH_2CO, 31H); 3.80 ppm (m, CH_2NCO, 2H); 4.00 ppm (m, CH_2NCO, 2H); 4.55 ppm (s, AnthCH_2N, 2H); 6.60–8.60 ppm (m, ArH, 13H). MS (LSIMS), *m/z* 741 (73%, $(M + Na)^+$); 719 (100%, $(M + H)^+$); 718 (54%, $(M)^{+\bullet}$); 529 (24%).

2.2.2. Probe A2

1-Iodo-3,6-dioxaheptane is prepared by refluxing for 40 h a mixture of NaI (240 mmol) and 3-chloro-3,6-dioxaheptane (79 mmol) in acetone (100 ml). Chloroform (150 ml) is added and the organic phase is treated with a solution of $Na_2S_2O_3$ (5%) and washed with water. After drying, the organic phase over sodium sulfate and evaporation under vacuum, the iodo derivative is obtained as a yellow liquid (yield 89%). IR (NaCl film), ν, 2875; 1455; 1355; 1265; 1200; 1170; 1135; 1110; 1035; 980; 850; 755; 655 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ, 3.20 ppm (t, 2H); 3.31 ppm (s, 3H); 3.40–3.60 ppm (m, 4H); 3.68 ppm (t, 2H).

Methyl 4-(1′,4′,7′-trioxaoctyl)phenyl acetate is prepared by reaction of methyl (4-hydroxyphenyl) acetate (18 mmol) with 1-iodo-3,6-dioxa heptane (18 mmol) and K_2CO_3 (100 mmol) in acetonitrile (100 ml) at 100°C for 20 h under magnetic stirring. Chloroform (150 ml) is added and the organic phase is treated successively with a solution of $Na_2S_2O_4$ (5%, 100 ml)), NaOH (5%, 100 ml) and water (200 ml). After drying, the organic phase over sodium sulfate and evaporation under vacuum, the acetate is obtained as a yellow liquid (yield 96%). IR (NaCl film), ν, 2925; 2880; 1735; 1615; 1585; 1515; 1455; 1435; 1355; 1300; 1245; 1200; 1140; 1110; 1065; 1015; 925; 845; 820; 730; 665 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ, 3.40 ppm (s, 3H); 3.58–4.13 ppm (m, 13H); 6.80–7.20 ppm (m, 4H).

4-(1′,4′,7′-Trioxaoctyl)phenyl-2-ethanol is synthesized by action of $LiAlH_4$ (25 mmol) on methyl 4-(1′,4′,7′-trioxaoctyl)phenyl acetate (17 mmol) in THF (100 ml) at room temperature for 1 h and 1h at 80°C. Hydrolysis at 0°C with HCl (5%), extraction with dichloromethane and usual workup gives the alcohol as a liquid (yield 93%). IR (NaCl film), ν, 3430; 2925; 2875; 1610; 1585; 1510; 1455; 1355; 1300; 1245; 1200; 1180; 1135; 1110; 1065; 1050; 925; 845; 825; 730; 665 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ, 2.10 ppm (s, 1H); 2.78 ppm (t, 2H); 3.38 ppm (s, 3H); 3.56–4.10 ppm (m, 10H); 6.80–7.20 ppm (m, 4H).

1-Cyano-2- (2-(4-(1′,4′,7′-trioxaoctyl)phenyl)ethoxy)-ethane is prepared by stirring the preceding alcohol (16 mmol) and acrylonitrile (19 mmol) in presence of KOH (0.1 g) in water (1.5 ml) at 0°C for 4 h and at room temperature for 20 h. Dichloromethane (200 ml) is added to the mixture which is subsequently washed with water (100 ml). Usual workup allows the isolation of the cyano derivative as a liquid (yield 95%). IR (NaCl film), ν, 2930; 2875; 2250; 1610; 1585; 1510; 1455; 1420; 1355; 1300; 1245; 1200; 1180; 1110; 1065; 1050; 925; 845; 825; 735; 665 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ, 2.15–2.85 ppm (m, 4H); 3.23 ppm (s, 3H); 3.30–4.15 ppm (m, 12H); 6.30–7.00 ppm (m, 4H).

3-(2-(4-(1′,4′,7′-Trioxaoctyl)phenyl)ethoxy)propanoic acid is synthesized by refluxing 1-cyano-2- (4-(1′,4′,7′-trioxaoctyl)phenyl–2-ethoxy)ethane (15 mmol) in concentrated HCl (18 ml) for 2 h. Liquid-liquid extraction with dichloromethane for 40 h, workup of the organic phase and chromatography on silica gel (eluent: CH_2Cl_2/Et_2O (1v/1v) allow the isolation of the substituted propanoic acid (yield 53%). IR (NaCl film), ν, 3500–2500 cm^{-1} (large band); 1735; 1610; 1585; 1515; 1455; 1375; 1355; 1300; 1245; 1180; 1110; 1065; 925; 830; 665 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ, 2.15–3 ppm (m, 4H); 3.23 ppm (s, 3H); 3.30–4.15 ppm (m, 12H); 6.30–7.00 ppm (m, 4H); 7.90 ppm (s, 1H).

3-(2-(4-(1′,4′,7′-Trioxaoctyl)phenyl)ethoxy)propanoyl chloride is prepared by treating 3-(4-(1′,4′,7′-trioxaoctyl)-phenyl-2-ethoxy)propanoic acid (32 mmol) with oxalyl chloride (63 mmol) in benzene (30 ml) at reflux for 5 h under magnetic stirring. The organic solvents are evaporated under vacuum giving the acid chloride as a liquid (yield 100%).

N'-(3-(2-(4-(1′,4′,7′-Trioxaoctyl)phenyl)ethoxy)propanoyl)-*N*-benzyloxycarbonyl-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane is synthesized by reacting at room temperature for 20 h 3-(2-(4-(1′,4′,7′-Trioxaoctyl)phenyl)ethoxy) propanoyl chloride (1.6 mmol), *N*-benzyloxycarbonyl-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (1.0 mmol) and triethylamine (10 mmol) in benzene (40 ml). The mixture is treated by NaOH (10%, 10 ml) for 15 mn at room temperature and then the organic phase is washed successively with NaOH (10%, 20 ml) and HCl (10%, 40 ml). Usual workup gives the expected product as an oil (yield 93%). IR (NaCl film), ν, 2925; 2870; 1735; 1700; 1640; 1615; 1585; 1510; 1455; 1415; 1365; 1355; 1245; 1180; 1110; 1065; 925; 825; 770; 735 cm^{-1}. ^1H NMR ($CDCl_3$) δ, 2.53 ppm (t, 2H); 2.72 ppm (t, 2H); 3.31 ppm (s, 3H); 3.40–3.70 ppm (m, 32H); 3.76 ppm (t, 2H); 4.03 ppm (t, 2H); 5.04 ppm (s, 2H); 6.70–7.30 ppm (m, 9H).

N-(3-(2-(4-(1′,4′,7′-Trioxaoctyl)phenyl)ethoxy)propanoyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane is obtained by treating the preceding compound (0.54 mmol) with Pd/C (10%, 80 mg) and acetic acid (0.1 ml) in THF (50 ml) under hydrogen atmosphere (1 bar) for 40 h. After evaporation of the solvent, the residue is dissolved in chloroform (100 ml). The organic phase is washed with water (100 ml) and the aqueous phase, made alkaline (pH = 11) with NaOH (10%), is extracted three times with chloroform (50 ml). The chloroform phases are evaporated under vacuum and the residue chromatographed on neutral alumina (eluent: CH_2Cl_2/CH_3OH 95v/5v) giving the expected compound (yield 50%). IR (NaCl film), ν, 3455; 2920; 2870; 1735; 1640; 1615; 1580; 1455; 1355; 1300; 1245; 1200; 1180; 1110; 1065; 925; 830; 730 cm^{-1}. ^1H NMR ($CDCl_3$) δ, 2.54 ppm (t, 2H); 2.71 ppm (t, 4H); 3.31 ppm (s, 3H); 3.40–3.70 ppm (m, 30H); 3.76 ppm (t, 2H); 4.03 ppm (t, 2H); 6.70–7.10 ppm (m, 4H).

N′-(3-(2-(4- (1′,4′,7′- Trioxaoctyl)phenyl)ethoxy)propanoyl)-*N*-(9-anthrylmethyl)-1, 10-diaza-4,7,13,16-tetraoxacyclooctadecane: A2. The probe A2 was obtained by refluxing a mixture of the preceding amine (0.23 mmol), 9-chloromethylanthracene (0.25 mmol) and potassium carbonate (0.75 mmol) in 10 ml of acetonitrile for 20 h. After evaporation of the solvent under vacuum, dichloromethane (50 ml) is added to the residue. The organic phase is washed with water and chromatographed on neutral alumina (eluent: CH_2Cl_2/CH_3OH 98v/2v) giving the probe A2 as a deep yellow oil (yield 70%). IR (NaCl film), ν, 2920; 2870; 1725; 1640; 1615; 1510; 1455; 1355; 1300; 1285; 1245; 1200; 1180; 1110; 1065; 935; 890; 830; 735; 695; 665 cm^{-1}. ^1H NMR ($CDCl_3$) δ, 2.54 ppm (m, $C_6H_4CH_2$, 2H); 2.70 ppm (m, NCH_2, 4H); 3.30 ppm (s, OCH_3, 3H); 3.35–3.70 ppm (m, $OCH_2 + CH_2CON$, 30H); 3.75 ppm (m, CH_2NCO, 2H); 4.00 ppm (m, CH_2NCO, 2H); 4.47 ppm (s, $AnthCH_2N$, 2H); 6.50–8.60 ppm (m, ArH, 13H). MS (LSIMS), *m/z* 769 (85%, $(M + Na)^+$); 747 (100%, $(M + H)^+$); 746 (34%, $(M)^{+\bullet}$); 613 (34%); 557 (34%); 241 (19%); 240 (17%); 223 (33%); 222 (39%).

3. Results and discussion

The field of fluorescent sensors has developed to the point that a range of inorganic cation or small saccharides can now be targeted successfully [10,11]. The complexation of ammonium ion is well achieved by 18-crown-6 or 1,10-diazacrown-6 and has been studied quantitatively [12]. The presence of cation π interactions are now known to play important roles in the stabilization of complexes between quaternary ammoniums and synthetic receptors that contain an electron-rich aryl part [13].

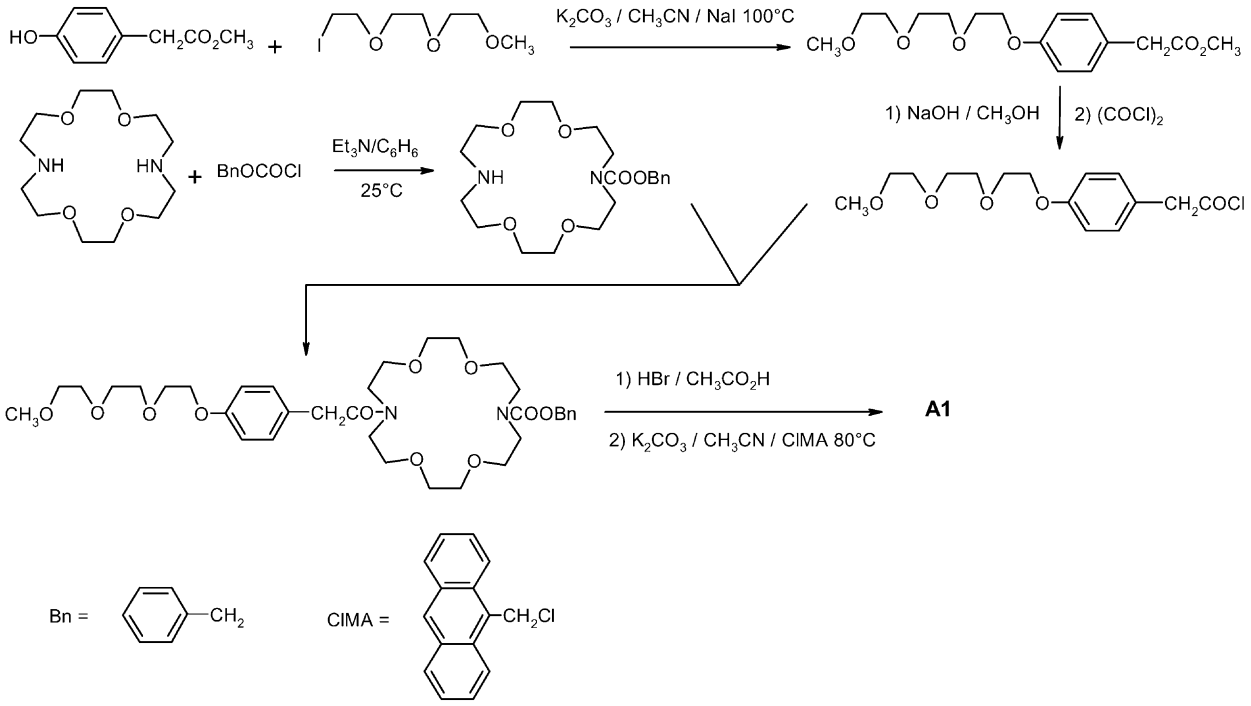
3.1. Probes A1 and A2

The above considerations led us to synthesize the probes A1 and A2. They contain a 9-anthrylmethyl moiety, as fluorescent sensor, a 1,10-diazacrown-6 entity bearing a complexing side arm with a phenylene group to increase the ammonium binding properties. The amino group of the complexing part of the probes, linked to the anthracene entity, deactivates its fluorescence by photoinduced electron transfer mechanism [10]. When an ammonium group is complexed by the crown ether, the quenching of the fluorescence by the amino group is less, and its intensity increases. Such fluorescence intensity enhancement has been already used by one of us for specific cation recognition [14].

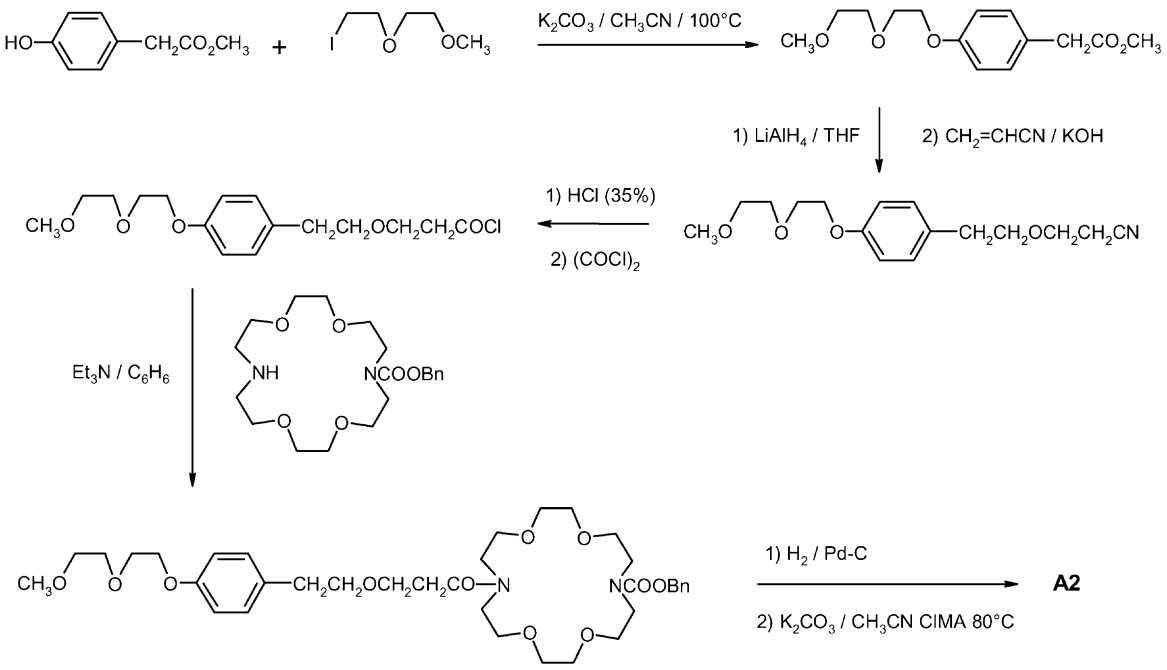
The synthesis of the probes A1 and A2, involving classical methods of the organic chemistry, are given in Schemes 1 and 2, respectively (see experimental part). It is remarkable that in the synthesis procedure to prepare A1, the step of deprotection of the benzyloxycarbonyl, performed using bromhydric acid, leads a demethylation of the polyethylene oxide chain.

The fluorescence properties of the probes were evaluated in methanol as solvent using a commercial potato cationic starch Hi-Cat 180 from Roquette (France). The cationic starch, which presents a nitrogen concentration of 0.65%, was dissolved in water at pH = 6 (concentration 1% by weight) and the fluorescence emission in the absence and in presence of Hi-Cat was compared for the two probes (Fig. 1). As expected, a large enhancement of the fluorescence intensity is observed for both compounds with a larger one for A2. This is in accordance with a better ability for the side arm to contribute to the complexation of the ammonium group, as revealed by molecular models.

The selectivity of complexation for the ammonium group is revealed in Fig. 2 where Na^+, K^+ and Ca^{2+} do not



Scheme 1. Synthesis of the probe A1.



Scheme 2. Synthesis of the probe A2.

bring an increase of the fluorescence intensity. Moreover, it was checked that starch without ammonium groups does not have any influence on the fluorescence intensity of the probes. The fluorescence enhancement intensity was not found to correlate linearly with the ammonium concentration. One more drawback of the use of the probes A1 and A2 is the necessity to operate in organic solvent, such as methanol because the fluorescence enhancement was found much lower in water (results not shown) due to the solvation of the amino group by the water which prevents strong

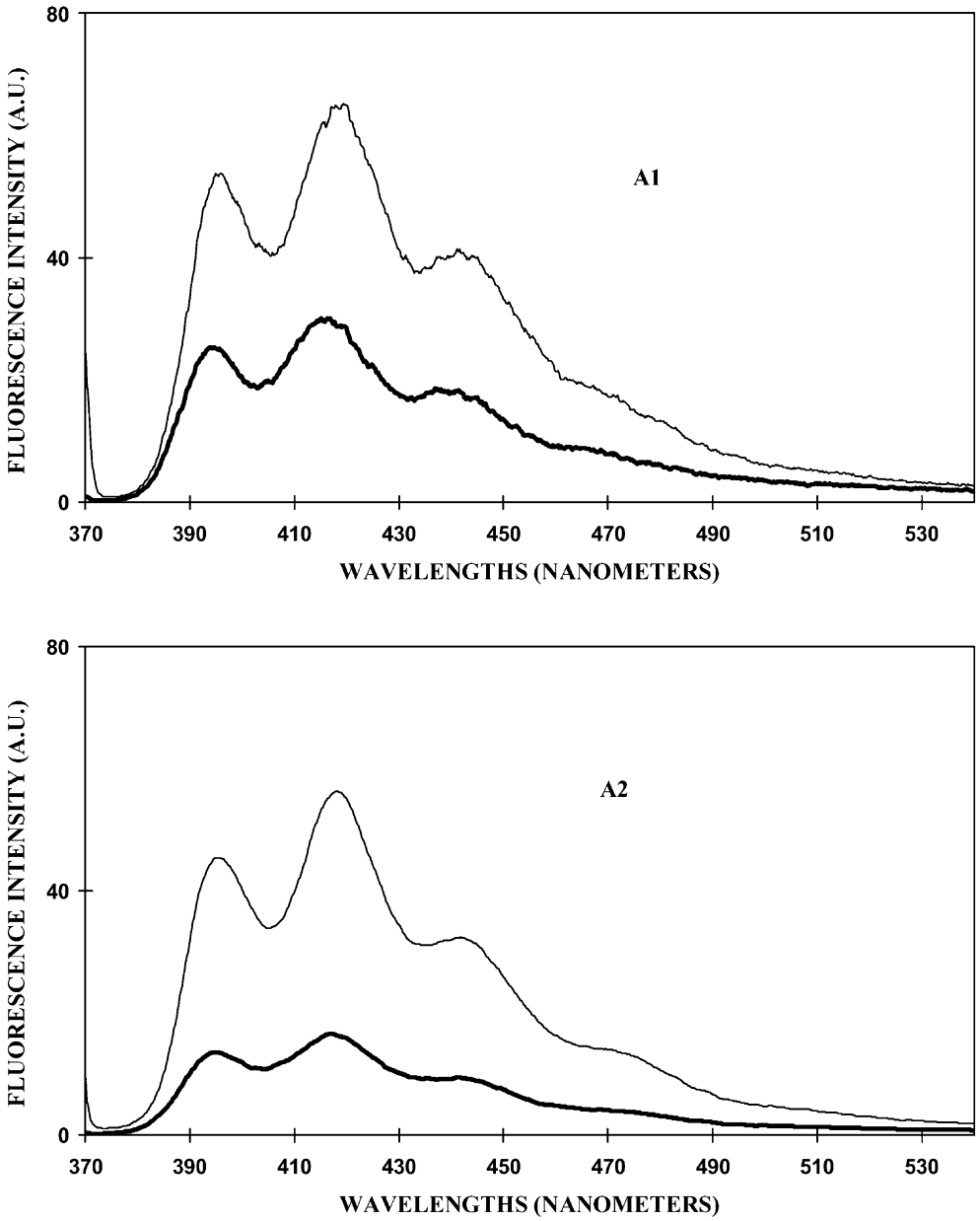


Fig. 1. Fluorescence spectra of the probes A1 and A2 (concentration $\approx 10^{-5}$ mol l^{-1}) in undegassed methanol (λ_{exc}: 365 nm; f_{exc}: 2.5 nm; f_{em}: 5 nm) in absence of cationic starch (—) and in presence of cationic starch Hi-Cat 180 (3.8×10^{-5} mol l^{-1} of ammonium) (—).

donor-acceptor interaction between the amine and the anthracene ring.

3.2. Fluorescent whitening agent (FWA)

Due to the difficulties to quantify the amount of cationic starch in water solution with the probes A1 and A2, we have looked for other probes working in water. We have found that FWA, which absorbs UV energy and reemits, at longer wavelength, blue light are sensitive to the presence of cationic starch in water solution. Crouse and Snow [15] have previously noted a quenching by cationic polymer of the fluorescence emitted by whitening agents in paper. This effect is due to the interaction between the anionic part of the FWA and ammonium groups that tend to agglomerate by electrostatic interactions. We have use a commercial FWA from Bayer: Blankophor PC which is a diaminostilbene tetrasulfonic acid.

The effect of the presence of cationic starch on the absorption of FWA in dilute water solution (pH = 4.5), shown in Fig. 3(A), is minor. In particular, the absorbance at 365 nm remains constant. We have chosen this wavelength for the excitation of the fluorescence of FWA in presence of various amount of cationic starch Hi-Cat 180, which are expressed

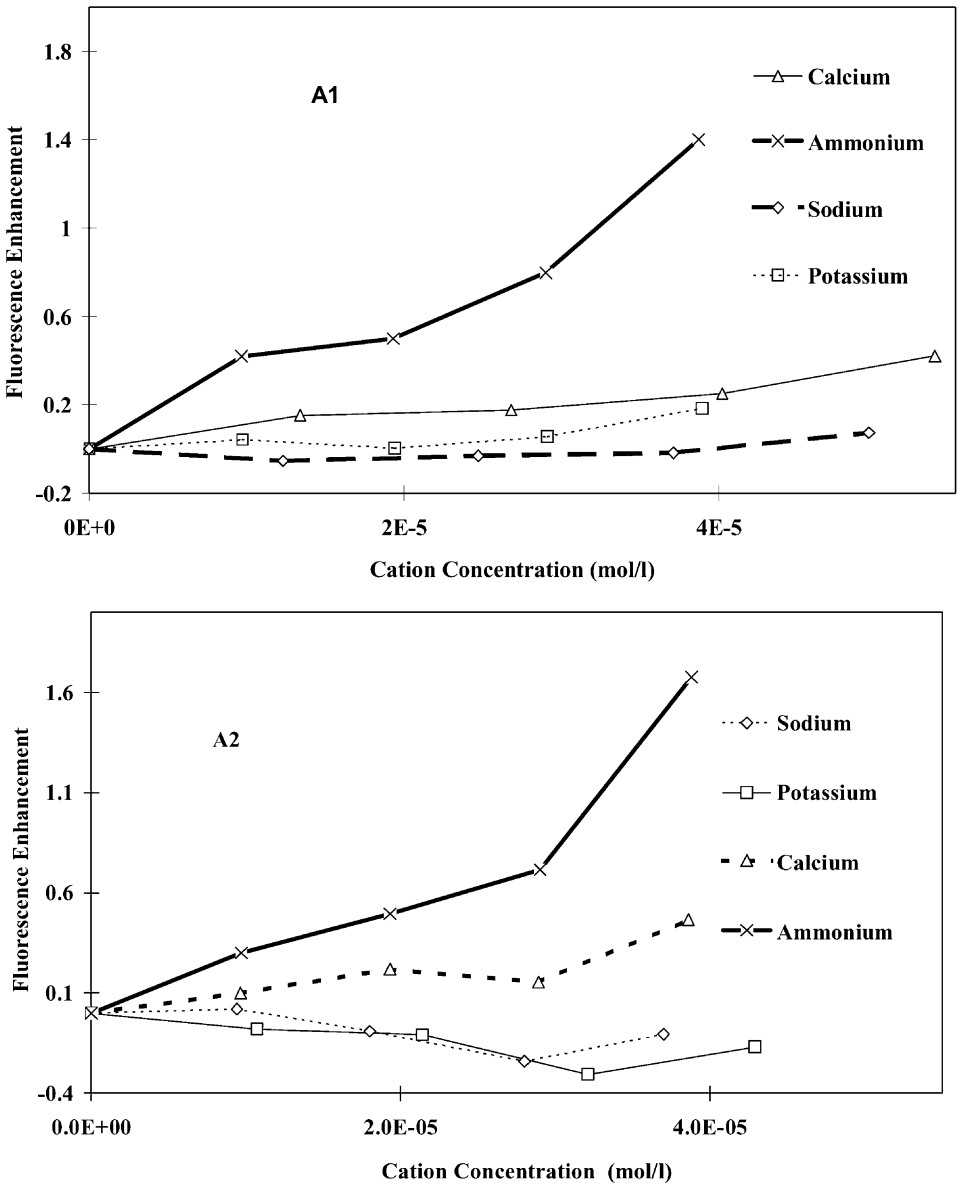


Fig. 2. Effect of the presence of cations on the fluorescence intensity of A1 and A2 (concentration $\approx 10^{-5}$ mol l^{-1}) in undegassed methanol (λ_{exc}: 365 nm; f_{exc}: 2.5 nm; f_{em}: 5 nm).

as molar ammonium concentration (Fig. 3(B)). The fluorescence spectra are very dependent on the starch concentration with a red shift of the spectrum as the cationic part increases. A linear relationship is found between the fluorescence intensity and the ammonium concentration with a very good correlation coefficient (0.998). No change in the fluorescence spectrum was noted when non-cationic starch is added to an aqueous solution (pH = 4.5) of FWA (results not shown). This indicates that the carbohydrate starch backbone has no effect on the fluorescence spectrum of FWA, and that the red shift noted has to be attributed to interaction between the ammonium groups and the aminostilbene sulfonates.

Other cations, such as magnesium (Fig. 4(C)) do not modify the fluorescence emission even though sodium, potassium and calcium have a slight effect (Fig. 4(A), (B) and (D)). By contrast, the presence of aluminum cation strongly affects the fluorescence emission of FWA (Fig. 4(E)).

The cation concentrations used in this study to detect interactions between the excited singlet state of FWA and the cations are in the order of those use in the water circuit of the head box of a paper machine. The response of FWA appears to fulfil the conditions for the determination of the concentration of cationic starch in the water circuit of a paper machine if the latter do not present absorption at 365 nm (presence of soluble lignin residues) and other type of cationic polymer, such as polyamine or polyamides. The practical application of this concept is being developed.

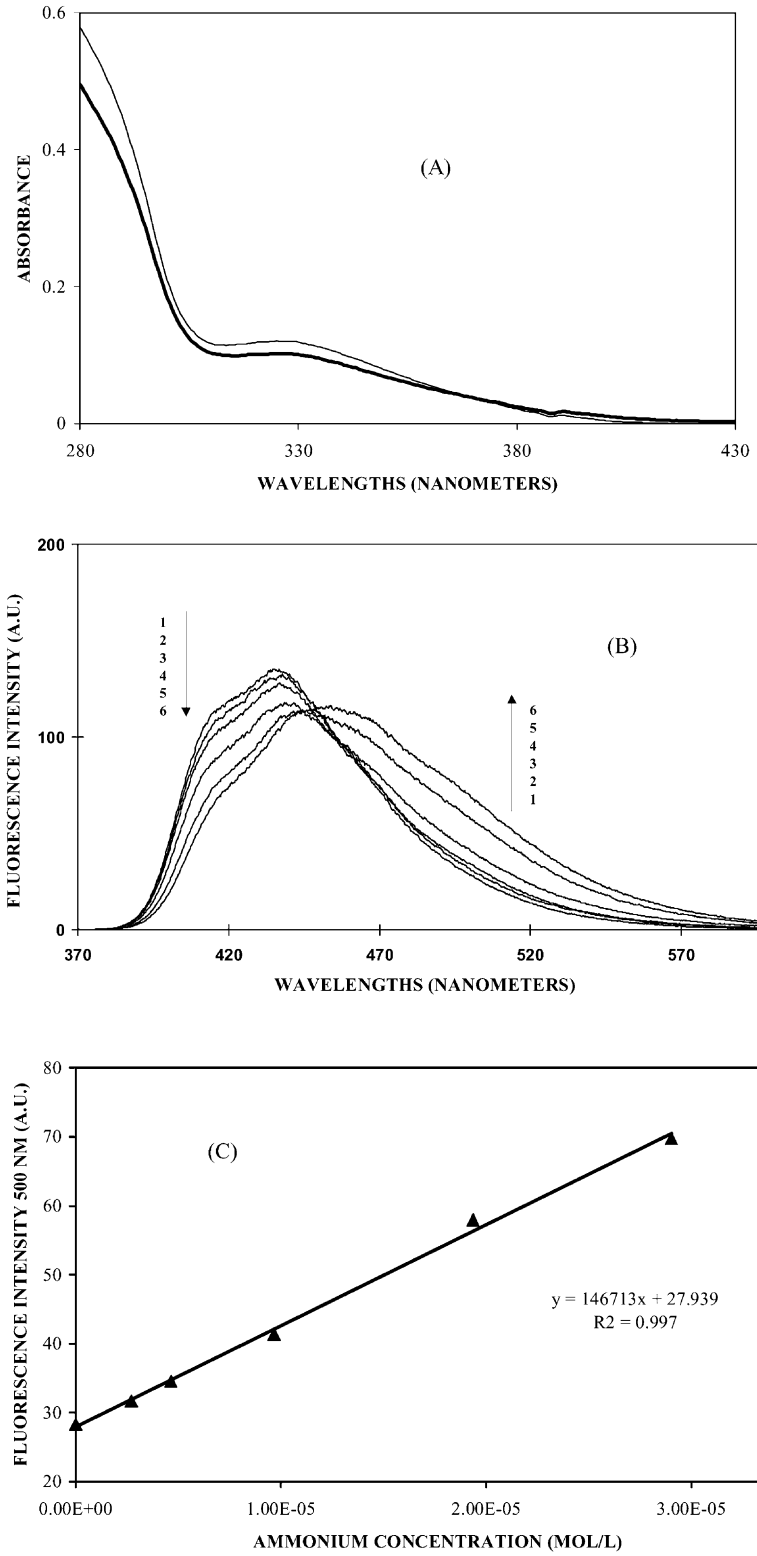


Fig. 3. (A) absorption spectra of the probe FWA in water (pH = 4.5) in absence of cationic starch (—) and in presence of cationic starch Hi-Cat 180 (7.7×10^{-6} mol l^{-1} of ammonium) (—). (B) Fluorescence spectra of the probe FWA in water (pH = 4.5); absorbance 365 nm ≈0.1; λ_{exc}: 365 nm; f_{exc}: 2.5 nm; f_{em}: 5 nm for various concentration of cationic starch Hi-Cat 180: (1) 0×10^{-6}; (2) 2.7×10^{-6}; (3) 4.6×10^{-6}; (4) 9.7×10^{-6}; (5) 19.4×10^{-6}; (6) 29.0×10^{-6} mol l^{-1} of ammonium. (C) Fluorescence intensity at 500 nm vs. ammonium concentration (see (B)).

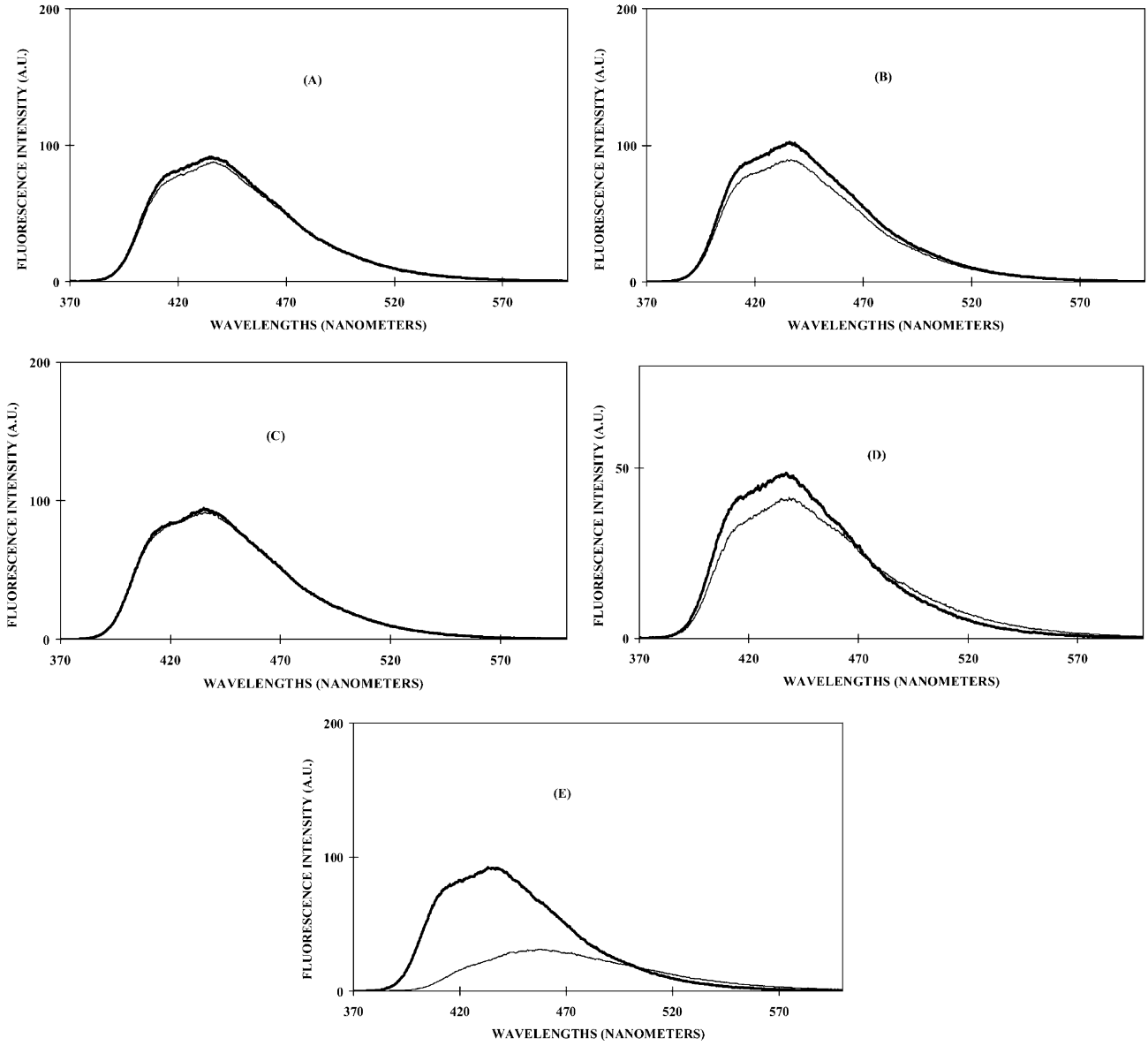


Fig. 4. Fluorescence spectra of the probe FWA in water (pH = 4.5); absorbance 365 nm ≈0.1; λ_{exc}: 365 nm; f_{exc}: 2.5 nm; f_{em}: 5 nm) in absence (—) and presence of cations (—). (A): Na^+ (412 ppm); (B): K^+ (46 ppm); (c) Mg^{++} (25 ppm); (D) Ca^{++} (2000 ppm); (E) Al^{+++} (12 ppm).

4. Conclusion

In present study, we have to designed and synthesized two fluorescent sensors which complex selectively ammonium group, grafted to starch, in polar organic solvents, such as methanol. Nevertheless the response was poor in water which limits the applicability of the probe to determine the concentration of cationic starch in water. By contrast, it was found that these conditions are fulfilled by a commercial aminostilbene sulfonate usually used as a fluorescent whitening agent for paper. This type of compound is very easy to find in the paper industry and the practical applicability of the method is under development in our Laboratory.

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