Chemical Physics Letters 501 (2011) 547–553

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Changes in fluorescent emission of cationic fluorophores in the presence of *n*-alkanes and alcohols in different polarity solvents

Arantzazu Delgado-Camón [a], Rosa Garriga [b,*], Elena Mateos [a], Vicente L. Cebolla [a], Javier Galbán [c], Luis Membrado [a], Susana de Marcos [c], Eva M. Gálvez [a]

[a] *Instituto de Carboquímica, CSIC, P.O. Box 549, 50080 Zaragoza, Spain*
[b] *Departamento de Química Física, Universidad de Zaragoza, 50009 Zaragoza, Spain*
[c] *Departamento de Química Analítica, Universidad de Zaragoza, 50009 Zaragoza, Spain*

ARTICLE INFO

Article history:
Received 17 July 2010
In final form 3 November 2010
Available online 6 November 2010

Keywords:
Berberine
Coralyne
Squarylium III
Fluorescence intensity changes
Non-specific interactions
Solvent polarity
Ion pairing
Reversed micelles

ABSTRACT

Berberine and coralyne experience either fluorescence enhancement or quenching when long hydrocarbon chain compounds (e.g., *n*-alkanes or alcohols) are added to their solutions, depending on solvent polarity. In polar solvents, as methanol or acetonitrile, the added compounds provide an apolar microenvironment that hinders alternative relaxation mechanisms, favouring fluorescence emission. However, alkane additions produce quenching in dichloromethane, which has been explained taking into account ion pairing between cationic fluorophore and counterion. The strong quenching measured after alcohol additions in dichloromethane suggests reversed micelle formation. Procedures and results described here may find practical applications in the development of analytical methods.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The effect of the medium on fluorescence, *i.e.* interactions between the fluorophore, analyte and solvent, is a key issue for the development of optical detection methods based on that property [1]. Non-specific, electrostatic interactions play an important role on fluorescent emission. It was found that a wide number of compounds induce changes, either increases or quenching, in the fluorescence of berberine or coralyne cations, that exclusively affect the emission intensity [2,3]. Likewise, it was reported that long hydrocarbon chain compounds produce high increases in emission when added to a silica gel plate which was previously impregnated with coralyne or berberine cation. A sensitive detection and quantification of alkanes (ng) and other nonfluorescent analytes (*e.g.*, lipids) was developed for Thin-Layer Chromatography, using fluorophore-impregnated silica gel plates [4–7][1]. A computational study, based on molecular orbital theory and molecular mechanics, showed that berberine cation and an alkane, as examples of fluorophore and chromophore-free molecule, respectively, establish a weak, non-specific electrostatic interaction which is responsible of the observed increase in emission intensity obtained in the polar silica gel solid medium [2,3].

Although the interactions involved are weak, it seems possible to tailor detection systems based on this phenomenon in liquid media for detecting different kinds of nonfluorescent compounds, with low UV response. Thus, a systematic study is presented here in which cationic fluorophores (berberine and coralyne) and also zwitterionic (squarylium III), are compared, before and after addition of a series of *n*-alkanes and alcohols[2], in solvents with different polarity[3]. Methanol (MeOH) and acetonitrile (ACN) have been selected as polar solvents, and dichloromethane (DCM) as apolar medium. Different mechanisms involved in fluorescence changes are proposed here, depending on solvent polarity and properties of the analyte added. Thus, this work addresses issues of theoretical and practical relevance in fluorescence spectroscopy.

---

* Corresponding author.
E-mail address: rosa@unizar.es (R. Garriga).

[1] Silica gel Thin-Layer Chromatographic (TLC) plates were impregnated using a methanolic solution of berberine or coralyne. After methanol removal, the nonfluorescent compounds were applied on the plate and submitted to chromatographic development. After removal of eluants, the compounds were detected using fluorescence densitometry by excitation at 365 or 410 nm, respectively (emission in the $\lambda > 450$ nm region). For details, see Refs. [6,7].

[2] Dielectric constants, at 20 °C, from Ref. [8]: *n*-pentane ($\varepsilon = 1.844$), *n*-decane ($\varepsilon = 1.991$), *n*-dodecane ($\varepsilon = 2.014$), *n*-hexadecane ($\varepsilon = 2.06$, at 25 °C), 1-butanol ($\varepsilon = 17.8$), 1-pentanol ($\varepsilon = 13.9$, at 25 °C), 1-hexanol ($\varepsilon = 13.3$, at 25 °C), 1-decanol ($\varepsilon = 8.1$), 2-dodecanol ($\varepsilon = 5.8$, at 30 °C, from Ref. [9]).

[3] Dielectric constants, at 20 °C, from Ref. [8]: methanol ($\varepsilon = 33.62$), acetonitrile ($\varepsilon = 37.5$), dichloromethane ($\varepsilon = 9.08$).

0009-2614/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2010.11.004

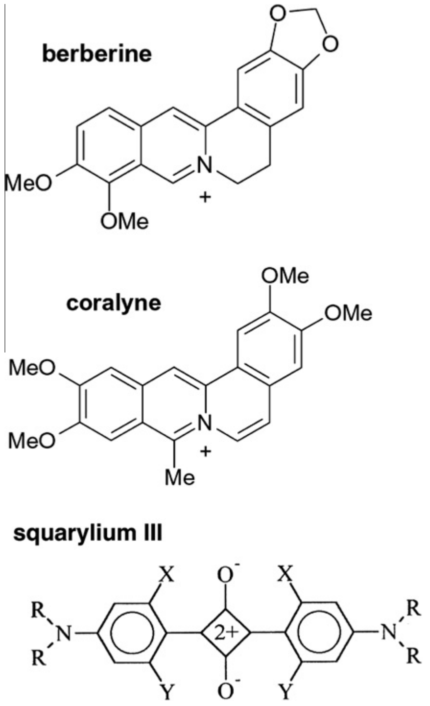

Figure 1. Chemical structures of fluorophores coralyne and berberine cations, and squarylium III (X = H, Y = H, R = CH_3).

2. Experimental

2.1. Materials

Berberine chloride (633-65-8 CAS) and berberine hemisulfate salt (95%+; 633-66-9 CAS) were purchased from Sigma–Aldrich Inc. (Saint Louis, USA); coralyne chloride hydrate (98%+; 38 989-38-7 CAS) was from Acros (Geel, Belgium); squarylium dye III (90% +; 43 134-09-4 CAS; 1,3-Bis[4-(dimethylamino)-phenyl]-2,4-dihydroxycyclobutenediylium dihydroxide, bis inner salt) was from Aldrich Chem. Co. (WI, USA). These fluorophores were used as received, and kept in darkness. Their molecular structures are depicted in Figure 1.

UVASOL® solvents dichloromethane (DCM), methanol (MeOH) and acetonitrile (ACN) for spectroscopy from Merck KGaA (Darmstadt, Germany) were used.

The following compounds were used for additions: *n*-pentane (99%; 8031-35-4 CAS); 1-butanol (99.8%; 71-36-3 CAS); and 2-dodecanol (99%; 10 203-28-8 CAS), from Sigma–Aldrich Inc., St. Louis, USA; *n*-decane, (>98%; 124-18-5 CAS), *n*-dodecane (>98%; 112-40-3 CAS), *n*-hexadecane (>98%, 544-76-3 CAS), 1-hexanol (>99%; 111-27-3 CAS), 1-decanol (97%; 112-30-1 CAS), from Fluka (Steinheim, Switzerland).

2.2. Fluorescence measurements of fluorophore solutions

Steady-state fluorescence measurements were performed with a Yobin Ivon FluoroMax-P spectrophotometer (Horiba, Kyoto, Japan). The fluorescence intensities were measured in a quartz cell at λ_{exc} = 360 nm in the case of berberine chloride, and at 365 nm for berberine sulphate. Spectra were collected with slits[4] set at 5 nm for the excitation and emission in MeOH and ACN, and at 2 nm in experiments performed in DCM. For coralyne chloride, λ_{exc} = 410 nm, slits[4] were set at 2 nm for the excitation and emission in MeOH and ACN, and at 1 nm in DCM. The used solvents did not provide any significant signal in the fluorescence spectra. Measurements were performed at room temperature, 24 °C.

Bath sonication was used for 15 min to solubilize berberine and coralyne in DCM. Solutions of berberine and coralyne 1 $\mu g\ mL^{-1}$ in DCM, MeOH and ACN were used. Given that the fluorophore spectra in DCM change with time, solutions were prepared 24 h prior to measurement in order to ensure a stable value of fluorescence intensity. Similarly, sonication was used for 60 min to solubilize squarylium dye III in DCM, avoiding heating. This time, squarylium dye III solutions in DCM were prepared at 0.01 $\mu g\ mL^{-1}$ to avoid aggregation or inner filter effects. In this case, solutions were prepared 7 days before measurements. It has to be remarked that all experiments in this work were performed at fluorophore concentrations within the range in which fluorescence intensity exhibits linear concentration dependence. Solutions were always kept in darkness, and special attention was paid in all cases to avoid evaporation of DCM.

2.3. Fluorescence measurements involving addition of solutions of alkanes or alcohols

One milliliter-solutions of *n*-alkanes and alcohols were directly added to 2 mL-solutions of fluorophores in a quartz cell, and emission spectra were registered. In order to suitably compare the measured fluorescence changes, solutions of the different compounds were added to obtain in all cases the same final concentration (1.115 M), unless otherwise stated.

Concerning fluorescence measurements, it was verified in each case that the light passed through the solutions before and after the additions. I_0 and I refer to the fluorescence intensity before and after the addition, respectively. I_0/I values at the maximum emission wavelength were calculated for each experiment from stable spectra, taking into account the corresponding concentration correction due to the dilution caused by addition.

Finally, in the case of 2-dodecanol additions in DCM, a study of fluorescence intensity evolution with time was performed for several days. Additionally, fluorescence measurements of a standard solution of quinine 1 $\mu g\ mL^{-1}$ in H_2SO_4 0.1 M were run together with the samples in order to correct fluctuations of the spectrophotometer lamp intensity after being switched off and on.

2.4. Other measurements

Refractive index *n* of all tested solutions, before and after the addition, were measured at room temperature 24 °C with an Abbe refractometer (Atago, Tokyo, Japan). Only three digits after decimal point are given due to the difficulty in performing fluorescence measurements using very volatile solvents such as DCM.

3. Results

Figure 2 shows the stable fluorescence emission spectra of berberine and coralyne chloride at concentration 1 $\mu g\ mL^{-1}$ in MeOH, DCM, and ACN, measured in the same experimental conditions in all cases (slits 2 × 2 nm). Berberine dyes in DCM give higher fluorescence emission intensity than that obtained in MeOH and ACN, and the contrary occurs to coralyne. Likewise, emission intensity of coralyne is higher than that of berberine in MeOH and ACN, and of the same order in DCM.

3.1. Results of additions in polar solvents

Only four compounds (*n*-pentane, 1-hexanol, 1-decanol and 2-dodecanol) were added to fluorophore solutions in MeOH.

---

[4] Except in experiment corresponding to Fig. 2.

Download English Version:

https://daneshyari.com/en/article/5384775

Download Persian Version:

https://daneshyari.com/article/5384775

Daneshyari.com