Signaling of water content in organic solvents by solvatochromism of a hydroxynaphthalimide-based merocyanine dye

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ABSTRACT

Determining the water content in organic solvents has attracted much research interest in view of its importance in various chemical processes. We investigated the signaling behavior of a benzothiazolium appended 4-hydroxynaphthalimide derivative **1** for the water content in water-miscible organic solvents such as tetrahydrofuran, acetone, dimethyl sulfoxide, acetonitrile, ethanol, and methanol using UV−vis and fluorescence spectroscopy. Probe **1** showed pronounced negative solvatochromism in common organic solvents and revealed excellent correlation between the $1/\lambda_{max}$ value and Reichardt's $E_T(30)$ parameter. The response to the changes in water content in the surveyed organic solvents could be analyzed using a ratiometric approach. The dependence of the absorption maximum (λ_{max}) on the changes in water content was also useful as a calibration plot. The fluorescence signaling behavior was less pronounced than that of the UV−vis signaling, but was still usable.

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1. Introduction

Determining and controlling the water content in various chemical systems is critical to a variety of chemical processes. Particularly, it is an important task in industries producing food, electronics, and fine chemicals [1]. In synthetic chemistry, the effective drying of solvents is often critical for water-sensitive reagents to ensure experimental reproducibility [2]. Because of its importance, the development of sensitive and convenient methods for water content determination in organic solvents is imperative for various chemical applications. For example, the water content in ethanol is an important parameter in the alternative fuel and pharmaceutical industries. Recently, ethanol has become an important alternative fuel, because in its hydrated form it is less harmful to the environment than traditional oil-based fuels [3]. However, the variation of water content in ethanol changes the physical and chemical properties of the fuel, which can cause increase in fuel consumption and damage automotive vehicle engines [4].

The water content in various substances such as common organic solvents, petroleum products, and foods is routinely determined using Karl Fischer titrations [5] or gas chromatography [6]. However, colorimetric or fluorescence methods are more

convenient than standard instrumental methods for routine laboratory activities. Numerous probes have been designed based on a variety of dyes and fluorophores. In fact, fluorescent sensors for the sensitive sensing of the water content in organic solvents have been successfully designed using various fluorophores of 1,8-naphthalimide [7,8], flavone derivatives [9], 8-hydroxyquinolines [10], 2,3-biphenyl quinoxaline 6-amine [11], and thioxanthone fluorophores [12]. The development of sensors based on fluorescent conjugated poly(m-aminobenzoic acid) [13], europium ternary complexes immobilized on glass surfaces [14], and acridine orange-based optical fiber [15] is also noteworthy. On the other hand, colorimetric sensors based on merocyanine dyes, such as various isomers of 4-[(4′-oxocyclohexa-2′,5′-dienylidene)ethylidene]-1,4-dihydropyridine [16,17] and hydroxycoumarin derived dyes [18], and using their unique solvatochromism have been reported. In addition to these, other sensitive sensors derived from various unique materials such as europium-based luminescent nanospheres [19] and a turn-on-type luminescent flexible Mg^{2+} metal-organic framework [20] have also been developed.

Solvatochromism is commonly used in many chemical and biological fields to investigate the bulk or local polarities of a macro-environment or to probe conformational changes and intermolecular interactions [21,22]. The solvatochromism of organic dyes is caused by non-specific (universal) and specific interactions of their molecules with solvent molecules [23]. Because

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the polarities of the ground and excited states of a dye are different, changes in the solvent polarity will lead to different stabilizations of the two states, which will eventually result in a change in the energy gap between these electronic states.

Merocyanine dyes contain two terminal heteroatoms with electron-donating and electron-accepting properties, as well as a polymethine chain [24]. The spectral properties of merocyanines are strongly dependent on their environment, including the polarity, viscosity, and presence of species capable of specific molecular interactions [25]. Because of these unique characteristics, they are often used in defining scales of solvent polarity [26], to determine water content in organic solvents, and as probes or markers in chemical analysis, biology, and medicine [27–29]. They are also used for the design of new materials and technologies such as non-linear optics [30], organic semiconductors [31], and electrochromism materials. Among other heterocycles such as indoles, benzoxazoles, and 2-dialkylaminothiophenes, benzothiazole moieties are one of the more widely employed subunits for the construction of merocyanine dyes [32–34].

The photophysical properties of naphthalimide derivatives are known to have a strong dependency on their environment [35]. In fact, 1,8-naphthalimide (NPI) has been commonly employed as a chromogenic or fluorescent signaling handle for both cation and anion sensing [36]. In particular, NPI fluorophores with a hydroxyl group on the naphthalene ring (NPI–OH) have been used for the construction of a number of colorimetric and/or ratiometric fluorescent chemodosimeters for Hg^{2+} [37,38], Pd^{2+} [39], F^- [40,41], thiols [42,43], and hydrogen sulfide [44,45]. In this paper, we report a novel colorimetric and fluorescent sensor for signaling the water content in common organic solvents such as acetonitrile, tetrahydrofuran (THF), ethanol, and methanol. The prepared merocyanine dye showed negative solvatochromism over a wide range of water concentrations. Ratiometric analyses of the spectral changes, as well as the extent of the wavelength shift in the absorption maximum (λ_{max}), were successfully used to determine the water content in various common organic solvents.

2. Experimental section

2.1. General

4-Bromo-1,8-naphthalic anhydride, 3-ethyl-2-methylbenzo thiazolium iodide, hexamethylenetetramine (HMTA), sodium methoxide, copper(II) sulfate, hydriodic acid, and all spectroscopic grade solvents were purchased from Aldrich Chemical Co. The ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were measured on a Varian VNS spectrometer and referenced to the residual solvent signals. UV–vis spectra were recorded with a Shinco S-3100 spectrophotometer. Fluorescence spectra were measured with a PTI QuantaMaster steady-state spectrofluorometer. Mass spectra (FAB) were obtained on a Micromass Autospec mass spectrometer. Compounds **3** and **4** were prepared following the reported procedures [46].

2.2. Preparation of 3-formyl-4-hydroxy-1,8-naphthalic-n-butylimide **5**

A mixture of 4-hydroxy-1,8-naphthalic-*n*-butylimide **4** (0.27 g, 1.0 mmol) and HMTA (0.28 g, 2.0 mmol) in trifluoroacetic acid (10 mL) was refluxed for 12 h, and then the solution was cooled to room temperature. The reaction mixture was diluted with distilled water, and the precipitates formed were filtered. The precipitates were washed with distilled water several times and dried. Subsequent dissolution in dichloromethane and purification using a short silica plug resulted in 3-formyl-4-hydroxy-1,8-naphthalic-n-

butylimide **5** (0.28 g, 95%). m.p.: 145.3–146.2 °C; ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 10.30 (s, 1H), 8.58 (d, J = 8.2 Hz, 1H), 8.55 (s, 1H), 8.47 (d, J = 7.1 Hz, 1H), 7.79 (t, J = 7.8 Hz, 1H), 3.96 (t, J = 7.4 Hz, 2H), 1.57 (p, J = 7.5 Hz, 2H), 1.34 (h, J = 7.4 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d$_6$) δ 194.5, 164.6, 163.5, 162.8, 133.9, 133.0, 131.4, 130.3, 127.4, 123.6, 122.6, 117.4, 113.8, 39.7, 30.1, 20.2, 14.2; HRMS: (FAB$^+$); m/z calcd for $C_{17}H_{15}NO_4^+$ [M]$^+$: 297.1001, found 297.1002.

2.3. Preparation of merocyanine dye **1**

3-Ethyl-2-methylbenzothiazolium iodide (0.92 g, 3 mmol) was added to a solution of 3-formyl-4-hydroxy-1,8-naphthalic-*n*-butylimide **5** (0.90 g, 3 mmol) in ethanol (20 mL). Pyridine (2.0 mL) was added to the solution, and then the mixture was stirred for 12 h at room temperature. After the reaction, the resulting solution was basified by 1 M NaOH to pH 11. The product was extracted using dichloromethane, and the combined organic solution was evaporated under reduced pressure. Crude products were purified using column chromatography (silica, eluent: dichloromethane:methanol = 9:1 *v/v*) to yield 1.1 g (62%) of merocyanine dye **1** as a brown powder. m.p.: >160 °C (decomposed); ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.52 (br d, J = 7.7 Hz, 1H), 8.29 (d, J = 7.3 Hz, 1H), 8.02 (br s, 1H), 7.70 (br s, 1H), 7.40 (t, J = 6.9 Hz, 1H), 7.30–7.21 (m, 3H), 7.09 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 8.2 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 4.04 (t, J = 7.5 Hz, 2H), 1.67 (p, J = 7.6 Hz, 2H), 1.51 (t, J = 7.2 Hz, 3H), 1.45 (h, J = 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 179.9, 170.2, 164.4, 163.6, 151.1, 140.2, 132.1, 131.9, 131.5, 131.5, 129.4, 128.0, 126.1, 126.0, 124.5, 122.2, 122.1, 118.6, 112.6, 106.8, 102.8, 42.8, 39.8, 30.4, 20.5, 13.9, 13.1; HRMS (FAB$^+$): m/z calcd for $C_{27}H_{25}N_2O_3S^+$ [M + H]$^+$: 457.1580, found: 457.1584.

2.4. Signaling of water content in organic solvents

Stock probe solutions were prepared by dissolving **1** in relevant organic solvents (5.0×10^{-4} M). Calculated amounts of water (0%–50%) and stock solution **1** were added to a vial. The resulting solution was diluted with the same solvent to make a final volume of 3.0 mL and final probe concentration of 2.0×10^{-5} M. The changes in the UV–vis and fluorescence spectrum were measured. To measure λ_{max}, the resolution of the UV–vis spectrophotometer was set at 0.2 nm.

2.5. Detection limit of water content

The detection limit was estimated by plotting the changes in the absorbance ratio at the two absorption maximums of the pure solvent and 50% aqueous solution $A_{(at\ \lambda_{max}\ of\ pure\ solvent)}/A_{(at\ \lambda_{max}\ of\ 50\%\ aqueous\ solution)}$ of **1** as a function of log [H$_2$O], following the reported procedure [47]. A linear regression curve was fitted to the values of the plot. The point at which this line crossed the ordinate axis was taken as the detection limit.

3. Results and discussion

Merocyanine dye **1** was prepared by a two-step reaction from 4-hydroxynaphthalimide **4** (Scheme 1). Compound **4** was prepared from 4-bromo-1,8-naphthalic anhydride **2** following the reported procedure [46]. The reaction of **2** with *n*-butylamine yielded a butylimide **3**. The methoxylation (NaOMe, CuSO$_4$/MeOH) of **3** (90%) followed by the cleavage of the methyl ether with hydriodic acid (HI) afforded **4** (60%). The formylation of **4** (HMTA, TFA) yielded an aldehyde **5** (95%), which was subsequently condensed with 3-ethyl-2-methylbenzothiazolium iodide to produce the desired merocyanine dye **1** (62%). The prepared product **1** had a