Dyes and Pigments 92 (2012) 1199–1203

Contents lists available at ScienceDirect

Dyes and Pigments

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

Chromogenic signalling of water content in organic solvents by hydrazone–acetate complexes

Youn Hwan Kim, Myung Gil Choi, Hyun Gyu Im, Sangdoo Ahn, Il Wun Shim, Suk-Kyu Chang*

Department of Chemistry, Chung-Ang University, Seoul 156-756, Republic of Korea

A R T I C L E   I N F O

Article history:
Received 20 February 2011
Received in revised form
11 July 2011
Accepted 19 July 2011
Available online 5 August 2011

Keywords:
Water content
Organic solvent
Hydrazone–acetate complex
Chromogenic signalling
Ratiometry
Probe

A B S T R A C T

New chromogenic probe systems for the signalling of the water content in representative water-miscible organic solvents (acetonitrile and tetrahydrofuran) were investigated. The effect of the water content in organic solvents on the complex formation of hydrazone dye with acetate ions was utilized for the signalling. The hydrazone–acetate system exhibited a pronounced chromogenic signalling behaviour that could be detected by eye in response to the changes in water content in such common water-miscible organic solvents as acetonitrile and tetrahydrofuran. Prominent colour changes were observed for up to 1 and 2% water content in acetonitrile and THF, respectively. Detection limits of the anthracene-based hydrazone–acetate system for determination of the water content in acetonitrile and tetrahydrofuran were 0.037 and 0.071%, respectively. The 7-hydroxycoumarin-based hydrazone–acetate system showed somewhat less sensitive signalling behaviour, with respective detection limits of 0.12 and 0.63% in acetonitrile and tetrahydrofuran. The designed hydrazone–acetate systems could be used as a simple and convenient chromogenic probes for the determination of the water content in representative organic solvents of acetonitrile and tetrahydrofuran.

1. Introduction

Determination of water content in organic solvents is very important in various fields of chemistry and industrial processes [1–5]. Water content in varying substances, such as common solvents, petroleum products, foods, and drugs are generally determined by Karl Fischer titration [6,7] or gas chromatography [8]. However, optical methods are more desirable than these conventional analytical techniques in terms of convenience and instrumental requirements. There have been many reports on the development of optical sensing systems employing various functional dye molecules [9,10] for the determination of water content in organic solvents, including merocyanines [11–13], flavones [14], chalcone [15], 3-hydroxychromone [16], naphthalimides [17,18], and indole derivatives [19].

Hydrazones are widely used in many fields of chemistry. In practical syntheses, hydrazones, acting as synthetic equivalents of the carbonyl compounds, are often preferred nitrogen analogues of aldehydes and ketones [20]. Hydrazones possessing an azomethine imine group constitute an important class of compounds for new drug development [21]. Hydrazone and its derivatives are also known to act as ligands for a variety of metal ions, including lanthanide(III) ions such as yttrium(III), lanthanum(III), and lutetium(III) [22–24]. For application towards metal ion binding, Sakamoto et al. reported the extraction of alkali metal ions by benzo-crown ethers bearing an ionizable hydrazone group [25]. More recently, metal–hydrazone complexes that exhibit vapochromic behaviour toward vapor molecules of alcohols, acetonitrile, dimethylformamide, dimethylsulfoxide, and 1,4-dioxane were investigated [26].

On the other hand, hydrazone derivatives are known to selectively interact with fluoride and acetate ions through hydrogen bonding [27]. There are many fluoride or acetate-selective hydrazone derivatives based on the various molecular framework of 5-bromosalicylaldehyde [28], indolin-2-one [29], 9-anthracenecarboxaldehyde [30], and 1,10-phenanthroline-2,9-dicarboxaldehyde [31]. A Ru(II)-based phenanthroline-5,6-dione containing a quinonehydrazone group that can be transformed to an azophenol form in the presence of fluoride ion has been reported [32]. However, due to the hydrogen bonding nature of the interaction, the recognition and/or sensing of the anions occurred only in noncompetitive organic solvents such as acetonitrile and DMSO [28]. In aqueous solution, the hydrogen bonding interaction between the hydrazone and fluoride or acetate was significantly weakened due to the presence of competing water molecules; the signalling thus became very weak or no longer possible [28].

---

* Corresponding author. Tel.: +82 2 820 5199; fax: +82 2 825 4736.
E-mail address: skchang@cau.ac.kr (S.-K. Chang).

0143-7208/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2011.07.019

We have designed a new chromogenic signalling system for the determination of the water content in organic solvents by using the effects of water on the complex formation of hydrazone with acetate ions. Among the acetate and fluoride chromogenic candidates for the hydrazone, acetate was chosen as a component of the probe system because hydrazones are known to interact with "Y"-shaped acetate ions more strongly than fluoride ions [30]. Using hydrazone–acetate complexes, variations in the water content in the water-miscible organic solvents of acetonitrile and tetrahydrofuran (THF) were sensitively visualized by ratiometry, as well as by visually discernible colour changes.

2. Experimental section

2.1. General

All solvents (acetonitrile, THF with 250 ppm 2,6-di-*tert*-butyl-4-methylphenol as inhibitor, and methanol) were purchased from Sigma–Aldrich Chemical Co. as 'anhydrous' grade. 9-Anthracenecarboxaldehyde, 7-hydroxycoumarin, 2,4-dinitrophenylhydrazine, trifluoroacetic acid (TFA), hexamethylenetetramine (HMTA), and tetrabutylammonium acetate were purchased and used without further purification. ^{1}H NMR (300 MHz, 600 MHz) and ^{13}C NMR (75 MHz, 150 MHz) spectra were obtained on a Varian Gemini-2000 and VNS spectrometer. Mass spectral data were obtained with a Micromass Autospec mass spectrometer. UV–vis spectra were recorded with a Jasco V-550 spectrophotometer. Compound **1** was prepared by the reaction of 9-anthracenecarboxaldehyde with 2,4-dinitrophenylhydrazine following the reported procedure [30].

2.2. Synthesis of 7-hydroxycoumarin-8-carboxaldehyde [33]

To a solution of 7-hydroxycoumarin (1.6 g, 9.9 mmol) in dichloromethane (20 mL) was added acetic anhydride (10.8 g, 106 mmol) and pyridine (15 μL). The reaction mixture was stirred at room temperature for 12 h and the volatiles were evaporated under reduced pressure. The residue was then dissolved in water, and extracted with ethyl acetate. The organic phase was separated, and washed with brine and water, and evaporated to obtain a solid residue. The product was purified by crystallization from ethyl acetate to yield 7-acetoxycoumarin. To a solution of 7-acetoxycoumarin (1.5 g, 7.35 mmol) in trifluoroacetic acid (10 mL) in an ice-cooled bath was added hexamethylenetetramine (1.5 g, 10.7 mmol). The reaction mixture was heated under reflux for 24 h. Volatiles of the reaction mixture were evaporated under reduced pressure, and water (30 mL) was added to the residue. The mixture was heated and stirred at 60 °C for half an hour. After cooling the mixture, the yellow precipitate formed was filtered and washed with water to give the 7-hydroxycoumarin-8-aldehyde as a yellow powder (1.06 g, 76% yield). mp 190 °C (decompose). ^{1}H NMR (300 MHz, DMSO–d_6) δ 10.28 (s, 1H), 7.76 (d, $J = 9.0$ Hz, 1H), 7.43 (d, $J = 8.7$ Hz, 1H), 6.46 (d, $J = 8.7$ Hz, 1H), 5.95 (d, $J = 9.0$ Hz, 1H). ^{13}C NMR (75 MHz, DMSO–d_6) δ 189.7, 173.3, 160.4, 158.4, 145.1, 134.2, 119.6, 111.0, 106.6, 105.7. IR (KBr); $\nu_{(O-H)}$ 3332, $\nu_{(C-H)}$ 3086, $\nu_{(C=O)}$ 1730 and 1656 cm^{-1}. HRMS (EI, DIP); *m*/*z* calcd for $C_{10}H_6O_4$ [M$^+$]: 190.0266, found 190.0265.

2.3. Synthesis of **2**

To a solution of 7-hydroxycoumarin-8-carboxaldehyde (190 mg, 1.0 mmol) in ethanol (10 mL) was added 2,4-dinitrophenylhydrazine (218 mg, 1.1 mmol); the reaction mixture was then heated under reflux for 5 h. After cooling to room temperature, the precipitate formed was filtered and washed with ethanol several times and dried under vacuum to yield a red powder, **2** (350 mg, Yield = 95%). Decompose at 230 °C. ^{1}H NMR (600 MHz, DMSO–d_6) δ 9.28 (s, 1H), 8.86 (d, $J = 3.0$ Hz, 1H), 8.39 (dd, $J = 3.0$ and 9.6 Hz, 1H), 8.01 (d, $J = 9.6$ Hz, 1H), 7.86 (d, $J = 9.6$ Hz, 1H), 7.66 (d, $J = 8.4$ Hz, 1H), 6.97 (d, $J = 8.4$ Hz, 1H), 6.34 (d, $J = 9.6$ Hz, 1H). ^{13}C NMR (150 MHz, DMSO–d_6) δ 160.8, 160.1, 153.7, 145.2, 145.0, 144.3, 137.7, 131.8, 130.4, 130.3, 123.4, 116.7, 113.8, 112.6, 112.0, 107.3. IR (KBr); $\nu_{(N-H \text{ and } O-H)}$ 3246, $\nu_{(C-H)}$ 3091, $\nu_{(C=O)}$ 1730, $\nu_{(C=N)}$ 1607, $\nu_{(NO_2)}$ 1506 and 1325 cm^{-1}. HRMS (EI, DIP); *m*/*z* calcd for $C_{16}H_{10}N_4O_7$ [M$^+$]: 370.0549, found 370.0594.

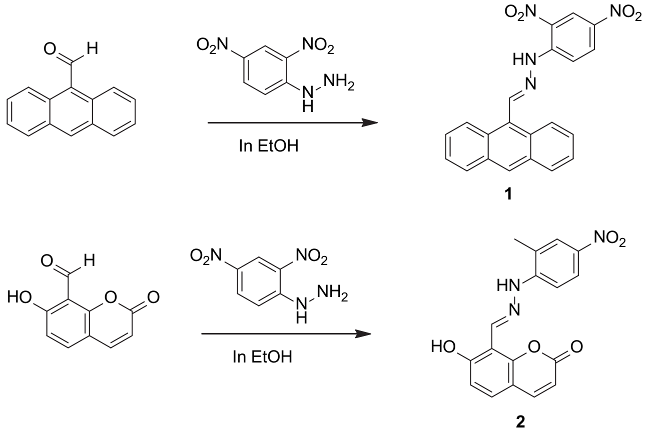
2.4. Titration experiments

Stock solutions of **1** and **2** were prepared in acetonitrile and THF. Solutions of hydrazone–acetate complex were prepared by respective addition of 10 equiv and 100 equiv of acetate ions to stock solutions of **1** and **2** in acetonitrile. In THF, 10 equiv of acetate ion was used to obtain the desired hydrazone–acetate complex. Final concentrations of **1** and **2** were 2.0×10^{-5} M in both solutions. Job's plot was obtained by plotting the absorbance at the maximum wavelength (536 nm for **1** and 502 nm for **2**), using varying amounts of 2.0×10^{-5} M of **1** or **2** and acetate ion under the conditions of: [hydrazone] + [acetate] = 2.0×10^{-5} M.

3. Results and discussion

The hydrazone derivative of anthracene aldehyde **1** was prepared by the reaction of 9-anthracenecarboxaldehyde with 2,4-dinitrophenylhydrazine in ethanol following the reported procedure [30]. Hydroxycoumarin-based hydrazone **2** was prepared similarly from 7-hydroxycoumarin-8-aldehyde, which was prepared by formylation of 7-hydroxycoumarin (HMTA, TFA) [33] (Scheme 1).

First, the UV–vis spectral behaviour of **1** in the presence of acetate ions in acetonitrile was measured. Hydrazone **1** showed strong absorption bands at 360 and 426 nm in acetonitrile (Fig. 1). Upon treatment with 100 equiv of acetate ion as the tetrabutylammonium salt, the absorption spectrum changed significantly; the absorption bands at 360 and 424 nm decreased while a new strong band at 536 nm developed. Concomitantly, the solution colour changed from yellow to red (left inset of Fig. 1). This chromogenic behaviour is, as is well-known, due to the complex formation by the hydrogen bonding interaction of **1** with acetate ions [30]. As shown in the right inset of Fig. 1, a constant signal was



Scheme 1. Preparation of hydrazone derivatives of anthracene and 7-hydroxycoumarin aldehyde.

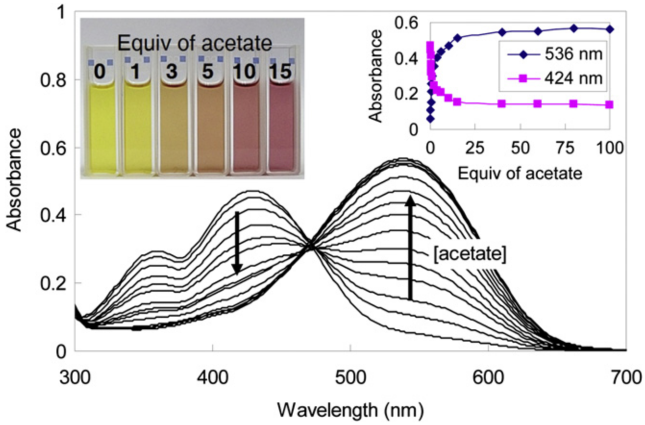


Fig. 1. UV–vis spectra of **1** and **1** in the presence of varying amount of acetate in acetonitrile. [**1**] = 2.0 × 10^{-5} M. Equiv of acetate = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, 10, 20, 40, 60, 80, and 100.

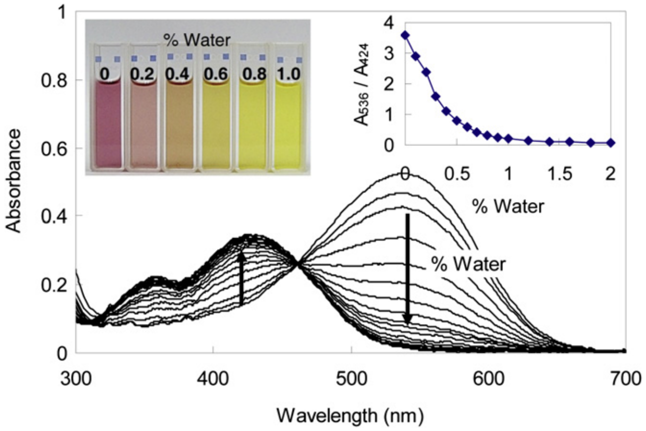


Fig. 2. Changes in UV–vis spectra of **1**–OAc system with varying water content in acetonitrile. [**1**] = 2.0 × 10^{-5} M, [OAc^-] = 2.0 × 10^{-3} M. Water % = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0.

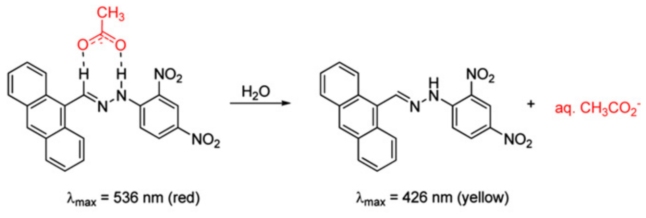
obtained with approximately 50 equiv of acetate ions. The Job's plot showed that the binding stoichiometry of **1** with the acetate ion was 1:1 (Figure S1, Supplementary data). From this change in the concentration-dependent UV–vis spectra, the association constant K_{assoc} for the **1**–OAc system in acetonitrile was estimated as 7.16 × 10^4 M^{-1} [34].

Next, the effect of the water content on formation of the **1**–OAc complex in acetonitrile was studied. When 5% water was added to the **1**–OAc system, which was obtained upon treatment of **1** with 100 equiv of acetate ions in acetonitrile, the UV–vis spectrum changed to nearly that of **1** only. This transformation was due to the breaking of the hydrogen bonding interaction between **1** and the acetate ions by water molecules (Scheme 2) [28]. In the presence of water molecules, the **1**–OAc complex was no longer stable and, upon dissociation of the acetate ions, free **1** was regenerated. This observation suggests that the chromogenic behaviour of **1**–OAc in response to the changes in water content could be used as a probe for signalling of water content in organic solvents.

Based upon this observation, a systematic investigation of the signalling of the water content in acetonitrile was executed. The changes in absorption behaviour of the **1**–OAc system, which was obtained by addition of 100 equiv of acetate ions to **1** (2.0 × 10^{-5} M), as a function of the water content in acetonitrile, were measured (Fig. 2). As the water content increased, the absorption behaviour was progressively converted from the spectrum of **1**–OAc to that of **1** only. Concomitantly, the solution colour progressively changed from red for **1**–OAc to yellow for free **1**; this could be easily discerned by eye.

The changes in the absorption spectrum of the **1**–OAc system as a function of water content could be conveniently analyzed by ratiometry using the ratio of the two absorbances at 536 and 424 nm. The plot of the absorbance ratio A_{536}/A_{424} as a function of the water content gave a well-correlated relationship (right inset of Fig. 2). Particularly, the changes in the lower water content region (<1%) were pronounced, and could be used as a calibration curve for determination of the water content in acetonitrile within this range. The response was quite pronounced and the transition of the solution colour from red to yellow in response to the changes in water content less than 1% could be easily discernible with the naked eye (left inset of Fig. 2). From this plot, the detection limit for determination of the water content in acetonitrile was estimated as 0.037%.

7-Hydroxycoumarin-derived hydrazone **2** also exhibited similar chromogenic signalling behaviour toward the water content in acetonitrile. Hydrazone **2** showed a strong absorption band at 385 nm in acetonitrile (Fig. 3). Upon treatment with 1 equiv of acetate as the tetrabutylammonium salt, the absorption spectrum changed significantly; the absorption band at 385 nm decreased while a new strong band at 502 nm developed. Concomitantly, the solution colour changed from yellow to red (left inset of Fig. 3). The strength of the complex formation of 7-hydroxycoumarin hydrazone **2** with acetate was found to be larger than that of anthracene derivative **1**, and the titration of **2** with acetate reached a saturation state much earlier (approximately 1 equiv of acetate ions) than **1**. The binding stoichiometry of the **2**–OAc system was also estimated to be 1:1 by a Job's plot (Figure S2, Supplementary data). From the



1-OAc

1

Scheme 2. Signalling of water content in organic solvents by the **1**–OAc system.

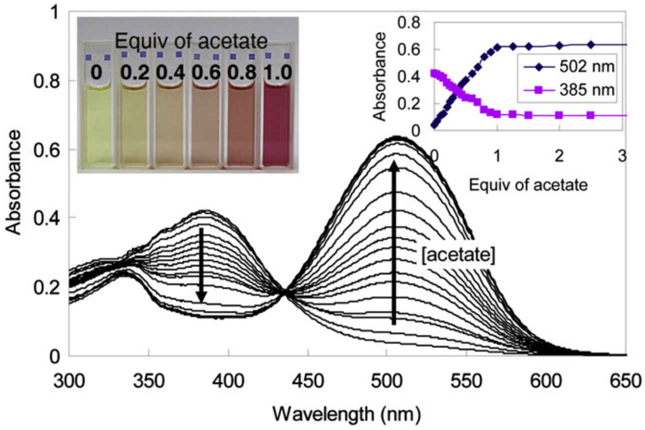


Fig. 3. UV–vis spectra of **2** and **2** in the presence of varying amounts of acetate in acetonitrile. [**2**] = 2.0 × 10^{-5} M. Equiv of acetate = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 5.0, and 10.

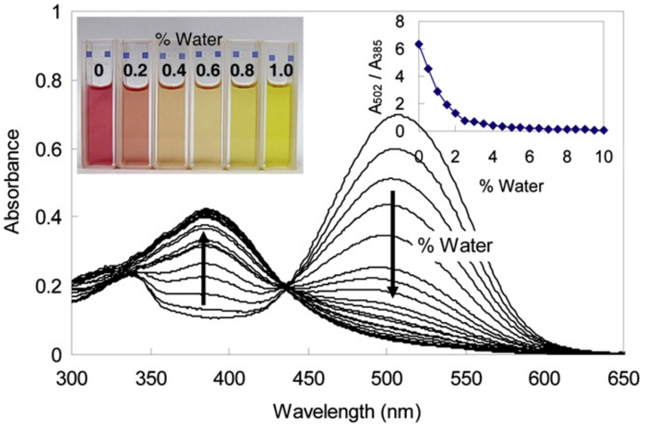


Fig. 4. Changes in UV–vis spectra of **2**–OAc system with varying water content in acetonitrile. [**2**] = 2.0 × 10^{-5} M, [OAc^-] = 2.0 × 10^{-4} M. Water % = 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, and 10.

concentration-dependent absorption changes, the association constant K_{assoc} of the **2**–OAc system was estimated to be 1.74×10^6 M^{-1} in acetonitrile. As other hydrazone sensors, although interference from fluoride might be present, coumarin based hydrazone **2** could function as a new sensor for the selective detection of acetate ions.

Next, the signalling of the water content in acetonitrile by the **2**–OAc system was investigated (Fig. 4). As the water content increased, the UV–vis absorption spectrum of **2**–OAc, obtained by treatment of **2** with 10 equiv of acetate ions in acetonitrile, changed steadily to that of **2** only. The solution colour concomitantly changed from red to yellow (left inset of Fig. 4). In this case, the ratiometric analysis afforded a good calibration curve for estimation of the water content up to 2% in acetonitrile. However, due to the difference in binding strength of **2**–OAc compared with **1**–OAc, somewhat different signalling behaviour was observed. A higher water content was required to convert the **2**–OAc system to **2**, and a prominent signalling useful for the determination of the water content was observed for up to 2% water. The detection limit of the **2**–OAc system for determination of the water content was 0.12% in acetonitrile.

To gain further insight into the signalling behaviour of the hydrazone–acetate system, the effect of the acetate concentration on the signalling of the water content in acetonitrile of the more stable **2**–OAc system was elucidated (Fig. 5). As the concentration of acetate increased from 2 to 10 equiv, the titration profile was affected slightly; increased amounts of acetate resulted in a slightly less sensitive response toward changes in the water content in acetonitrile. However, the titration results of the **2**–OAc system with the water content using 10 and 100 equiv of acetate were nearly identical. This implies that the signalling by the **2**–OAc system was relatively insensitive to the variations in acetate concentration between 10 and 100 equiv, which is favorable for practical application of the hydrazone–acetate signalling system. We used more than a stoichiometric amount of acetate for the complex formation of **1** or **2** with acetate ions. Although, the signalling sensitivity became somewhat lower when using excess acetate, the uncertainty introduced by using exact equivalent of acetate for the assay of water content would be mitigated as can be seen in Fig. 5.

Next, signalling of the water content in another important organic solvent THF was studied. Hydrazone **1** showed quite similar chromogenic behaviour toward the water content in THF, which is comparable to acetonitrile. Upon treatment with acetate ions, the absorption bands of free **1** at 359 and 426 nm in THF decreased steadily and a new strong band due to the **1**–OAc complex at 554 nm appeared (Figure S3, Supplementary data). As the water content in THF increased, the absorption spectrum of **1**–OAc progressively transformed to **1** only, with a prominent colour change from red to yellow that could be readily observed by eye (Fig. 6). Water signalling behaviour of **1**–OAc could be analyzed ratiometrically using the ratio of two characteristic absorbances at 554 and 426 nm (inset of Fig. 6). Significant changes in the absorbance ratio A_{554}/A_{426} were observed up to 1% water in THF. From the water content-dependent changes in A_{554}/A_{426}, the detection limit of the **1**–OAc system for determination of the water content in THF was estimated as 0.071%. Relevant signalling behaviour of the **2**–OAc system for probing water content in THF are given in the Supplementary data (Figures S4 and S5, Supplementary data).

Finally, the effect of polar impurities on the signalling of water by the present probe system was measured. Methanol was used as a representative polar impurity. In the presence of 0.5% methanol, significantly reduced responses were observed for **1**–OAc^- system in acetonitrile (Figure S6, Supplementary data). This observation is due to the fact that the present water signalling system is based upon the competition of water and acetate ions for the complex formation with the hydrazone chromophore by hydrogen bonding. Polar and strongly hydrogen bonding methanol molecules significantly interact with the hydrazone probe and affect the signalling of water content in acetonitrile.

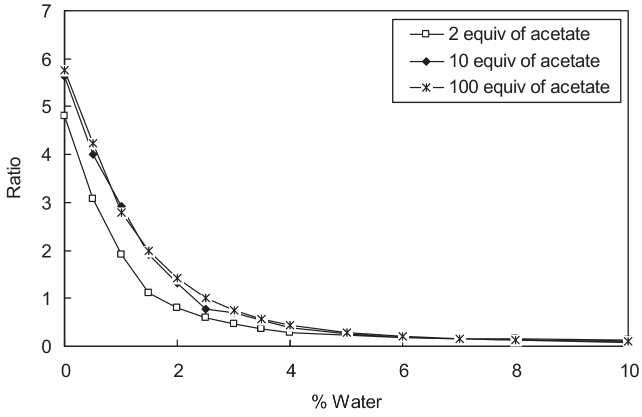


Fig. 5. Effect of acetate concentration on UV–vis titration of **2**–OAc system with water in acetonitrile. [**2**] = 2.0 × 10^{-5} M. Ratio = A_{502}/A_{385}.

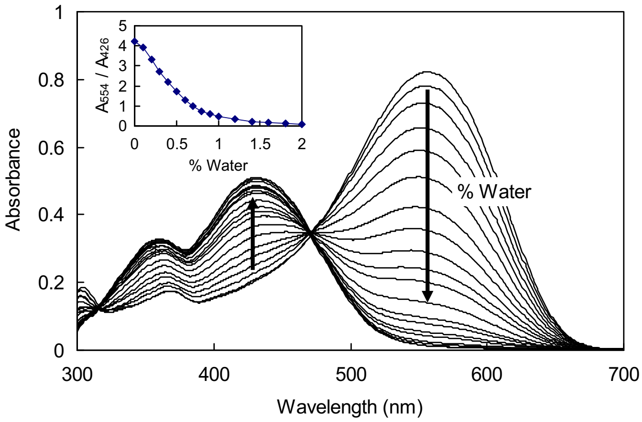


Fig. 6. Changes in UV–vis spectra of **1**–OAc system with water content in THF. [**1**] = 2.0 × 10^{-5} M, [OAc^-] = 2.0 × 10^{-4} M. Water % = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, and 10.

4. Conclusion

A new chromogenic signalling system for the determination of the water content in organic solvents was developed. Signalling was based on competition of water molecules with the hydrogen bonding interaction of acetate with hydrazone. Hydrazones were derived from 9-anthracenealdehyde and 7-hydroxycoumarin-8-carboxaldehyde. A pronounced chromogenic behaviour, detectable by eye, was observed for both compounds. The solution colour changed from red of the hydrazone–acetate complex to yellow of the hydrazone itself. Prominent colour changes were observed for up to 1 and 2% water content in acetonitrile and THF, respectively. The anthracene-based hydrazone was found to be more sensitive toward changes in water content than the 7-hydroxycoumarin derivative. The designed hydrazone–acetate system could be used as a convenient ratiometric probe for measurement of the water content in common water miscible organic solvents acetonitrile and THF.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2011.07.019.

References

[1] Hisamoto H, Tohma H, Yamada T, Yamauchi KI, Siswanta D, Yoshioka N, et al. Molecular design, characterization, and application of multi-information dyes for multi-dimensional optical chemical sensing. Molecular design concepts of the dyes and their fundamental spectral characteristics. Analytica Chimica Acta 1998;373:271–89.
[2] Timm RA, Falla MPH, Huila MFG, Peres HEM, Ramirez-Fernandez FJ, Araki K, et al. Vanadium oxide-porphyrin nanocomposites as gas sensor interfaces for probing low water content in ethanol. Sensors and Actuators B 2010;146:61–8.
[3] Wang Q, Li X, Wang L, Cheng Y, Xie G. Effect of water content on the kinetics of p-xylene liquid-phase catalytic oxidation to terephthalic acid. Industrial & Engineering Chemistry Research 2005;44:4518–22.
[4] Al-Zuhair S, Jayaraman KV, Krishnan S, Chan WH. The effect of fatty acid concentration and water content on the production of biodiesel by lipase. Biochemical Engineering Journal 2006;30:212–7.
[5] Nguyen TNP, Kim KJ. Transformation of monohydrate into anhydrous form of risedronate monosodium in methanol-water mixture. Industrial & Engineering Chemistry Research 2010;49:4842–9.
[6] Fischer K. Neues verfahren zur maßanalytischen bestimmung des wassergehaltes von flüssigkeiten und festen körpern. Angewante Chemie 1935;48:394–6.
[7] Kestens V, Conneely P, Bernreuther A. Vaporisation coulometric Karl Fischer titration: a perfect tool for water content determination of difficult matrix reference materials. Food Chemistry 2008;106:1454–9.
[8] O'Keefe WK, Ng FTT, Rempel GL. Validation of a gas chromatography/thermal conductivity detection method for the determination of the water content of oxygenated solvents. Journal of Chromatography A 2008;1182:113–8.
[9] Hisamoto H, Manabe Y, Yanai H, Tohma H, Yamada T, Suzuki K. Molecular design, characterization, and application of multiinformation dyes for multi-dimensional optical chemical sensings. 2. Preparation of the optical sensing membranes for the simultaneous measurements of pH and water content in organic media. Analytical Chemistry 1998;70:1255–61.
[10] Citterio D, Kawada T, Yagi J, Ishigaki T, Hisamoto H, Sasaki SI, et al. Molecular design, characterization, and application of multiinformation dyes for optical chemical sensing IV. Multiinformation dyes with extended spectral sensitivity in the near-infrared spectral range. Analytica Chimica Acta 2003;482:19–28.
[11] Kumoi S, Kobayashi H, Ueno K. Spectrophotometric determination of water in organic solvents with solvatochromic dyes-II. Talanta 1972;19:505–13.
[12] Gruda I, Bolduc F. Spectral properties and basicity of stilbazolium betaines containing bulky substituents on the quinoid ring. The Journal of Organic Chemistry 1984;49:3300–5.
[13] Lu H, Rutan SC. Solvatochromic studies on reversed-phase liquid chromatographic phases 1: synthesis and solvent effects of a new merocyanine dye, 4,6-dichloro-2-[2-(1-methyl-4-pyridinio)vinyl]-phenolate. Analytical Chemistry 1996;68:1381–6.
[14] Liu W, Wang Y, Jin W, Shen G, Yu R. Solvatochromogenic flavone dyes for the detection of water in acetone. Analytica Chimica Acta 1999;383:299–307.
[15] Niu CG, Guan AL, Zeng GM, Liu YG, Li ZW. Fluorescence water sensor based on covalent immobilization of chalcone derivative. Analytica Chimica Acta 2006;577:264–70.
[16] Ercelen S, Klymchenko AS, Demchenko AP. Ultrasensitive fluorescent probe for the hydrophobic range of solvent polarities. Analytica Chimica Acta 2002;464:273–87.
[17] Niu CG, Qin PZ, Zeng GM, Gui XQ, Guan AL. Fluorescence sensor for water in organic solvents prepared from covalent immobilization of 4-morpholinyl-1,8-naphthalimide. Analytical and Bioanalytical Chemistry 2007;387:1067–74.
[18] Li Z, Yang Q, Chang R, Ma G, Chen M, Zhang W. N-Heteroaryl-1,8-naphthalimide fluorescent sensor for water: molecular design, synthesis and properties. Dyes and Pigments 2011;88:307–14.
[19] Kim KN, Song KC, Noh JH, Chang SK. A simple phenol-indole dye as a chromogenic probe for the ratiometric determination of water content in organic solvents. Bulletin of the Korean Chemical Society 2009;30:197–200.
[20] Lazny R, Nodzewska AN. N-Dialkylhydrazones in organic synthesis. From simple N, N-dimethylhydrazones to supported chiral auxiliaries. Chemical Reviews 2010;110:1386–434.
[21] Rollas S. Küçükgüzel ŞG. Biological activities of hydrazone derivatives. Molecules 2007;12:1910–39.
[22] Dumitru F, Legrand YM, Barboiu M, Petit E, van der Lee A. Metallosupramolecular architectures of pseudoterpyridine-type ligands and Zn(II) metal ions. Crystal Growth & Design 2009;9:2917–21.
[23] Shuvaev KV, Abedin TSM, McClary CA, Dawe LN, Collins JL, Thompson LK. Ligand directed self-assembly vs. metal ion coordination algorithm—when does the ligand or the metal take control? Dalton Transactions; 2009:2926–39.
[24] Albrecht M, Mirtschin S, Osetska O, Dehn S, Enders D, Froehlich R, et al. Pentadentate ligands for the 1:1 coordination of lanthanide(III) salts. European Journal of Inorganic Chemistry 2007;20:3276–87.
[25] Sakamoto H, Goto H, Doi K, Otomo M. Compositional variation of ionizable crown ether-alkali metal ion complexes in the solvent extraction using several extraction solvents. Chemistry Letters 1992;8:1535–8.
[26] Kobayashi A, Dosen MA, Chang M, Nakajima K, Noro SI, Kato M. Synthesis of metal–hydrazone complexes and vapochromic behaviour of their hydrogen-bonded proton-transfer assemblies. Journal of the American Chemical Society 2010;132:15286–98.
[27] Gupta VK, Goyal RN, Sharma RA. Anion recognition using newly synthesized hydrogen bonding disubstituted phenylhydrazone-based receptors: poly(-vinyl chloride)-based sensor for acetate. Talanta 2008;76:859–64.
[28] Shao J, Lin H, Yu M, Cai Z, Lin H. Study on acetate ion recognition and sensing in aqueous media using a novel and simple colorimetric sensor and its analytical application. Talanta 2008;75:551–5.
[29] Shao J, Wang Y, Lin H, Li J, Lin H. A novel indole phenylhydrazone receptor: synthesis and recognition for acetate anion. Sensors and Actuators B 2008;134:849–53.
[30] Shang XF, Xu XF. The anion recognition properties of hydrazone derivatives containing anthracene. BioSystems 2009;96:165–71.
[31] Qiao YH, Lin H, Shao J, Lin HK. A highly selective naked-eye colorimetric sensor for acetate ion based on 1,10-phenanthroline-2,9-dicarboxyaldehyde-di-(p-substitutedphenyl-hydrazone). Spectrochimica Acta Part A 2009;72:378–81.
[32] Lin ZH, Ou SJ, Duan CY, Zhang BG, Bai ZP. Naked-eye detection of fluoride ion in water: a remarkably selective easy-to-prepare test paper. Chemical Communications; 2006:624–6.
[33] Lee KS, Kim HJ, Kim GH, Shin I, Hong JI. Fluorescent chemodosimeter for selective detection of cyanide in water. Organic Letters 2008;10:49–51.
[34] Kuzmič P. Program DYNAFIT for the analysis of enzyme kinetic data: application to HIV proteinase. Analytical Biochemistry 1996;237:260–73.