

Determination of Water Content in Aprotic Organic Solvents Using 8-Hydroxyquinoline Based Fluorescent Probe

Jun Soo Kim, Myung Gil Choi, Youn Huh, Mi Hee Kim, So Hee Kim, Se Yeon Wang, and Suk-Kyu Chang*

Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea *E-mail: skchang@cau.ac.kr

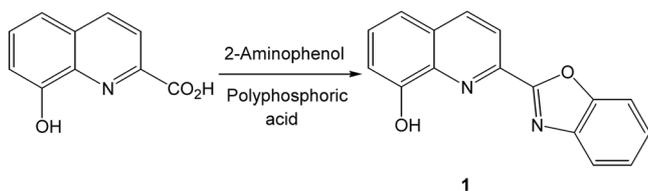
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Determination of water contents in organic solvents is important in routine chemistry laboratory and many practical applications in industrial processes.¹ There are a number of well established methods for the analysis of water contents in organic solvent systems, such as Karl Fischer titrations,² chromatography,³ and many other spectroscopic techniques.⁴ However, simpler and more convenient methods for the determination of water content are desirable in routine laboratory works and industrial processes. One of the most attractive methods is the spectroscopic technique using optical signaling systems such as chromogenic and fluorogenic devices.⁵⁻⁸ For the determination of water content in organic solvents, merocyanine dyes,⁹ flavone derivative⁴ and optical-fiber sensor employing acridine orange¹⁰ have been successfully utilized.

8-Hydroxyquinoline (8-HQ) and its related derivatives are known to have interesting metallochromism or metallofluorochromism.¹¹ The effects of environment on the fluorescence behavior of 8-HQ were well studied and the mechanism for the weak fluorescence of 8-HQ has been disclosed.^{12,13} The presence of water induces a strong fluorescence quenching of 8-HQ by the mechanism of radiationless relaxation. More recently, the origin of 'on-off' type fluorescent behavior of 8-HQ containing chemosensors was investigated in terms of PPT (photoinduced proton transfer) and PET (photoinduced electron transfer) processes.¹⁴ In this paper we report the chemosensing behavior of a simple organic compound based upon 8-HQ molecular framework for the determination of water content in common water miscible aprotic organic solvents. The compound exhibited sensitive responses toward the water content changes in aprotic solvents particularly in less than 2% water region.

Compound **1** was prepared by the reaction of 8-hydroxy-2-quinolinecarboxylic acid with 2-aminophenol (polyphosphoric acid, 150 °C) in good yield.¹⁵



We have performed systematic surveys to assess the ability of the compound in reporting the water content in a

series of common polar organic solvents of acetonitrile, THF, and dioxane. In acetonitrile solution, the compound **1** exhibited a broad emission spectrum centered at 463 nm with a minor shoulder around 530 nm (Figure 1). As can be seen from the Figure, compound **1** showed significant quenching of fluorescence with a small red shift ($\Delta\lambda = 4$ nm) in emission maxima as the water content increased. Particularly, the most dramatic changes were observed within lower water concentration range of less than 1%, which spans 92% of the total changes in fluorescence intensity observed at 463 nm. Above this concentration the fluorescence changes were relatively insignificant. The large changes in fluorescence intensity of **1** as a function of water content may be used as a new molecular probe for the determination of water content in acetonitrile solution.

In dioxane, changes in fluorescence profile and intensities as a function of water content were almost similar to the results from acetonitrile except for the wavelength of emission band. Compound **1** exhibited similar broad emission bands centered around 442 nm in dioxane. Upon addition of water the emission intensities were also decreased significantly with a small red shift ($\Delta\lambda = 5$ nm). The fluorescence intensity changes were also prominent particularly in lower water content region and the fluorescence quenching induced by 1% water was 73% of the total fluorescence changes for

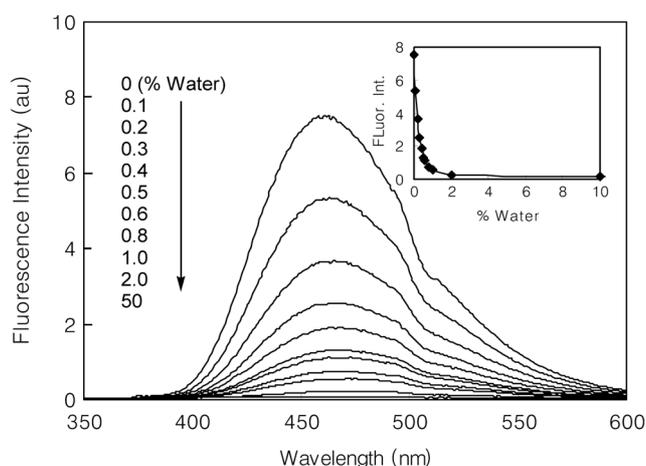


Figure 1. Changes in fluorescence intensities as a function of water content in aqueous acetonitrile solution. $[1] = 5.0 \times 10^{-5}$ M, $\lambda_{\text{ex}} = 340$ nm. Inset shows the profile for the fluorescence intensity at 463 nm as a function of water content.

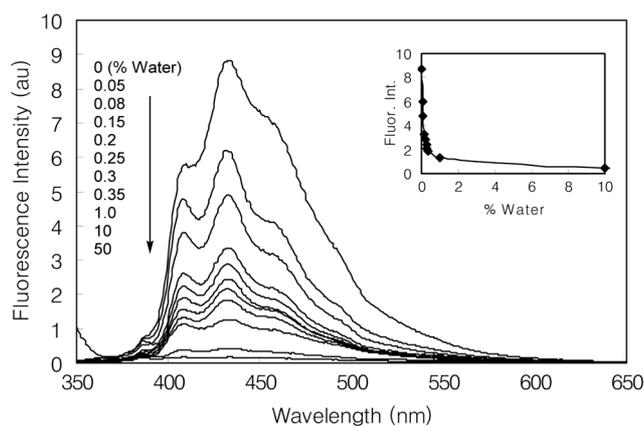


Figure 2. Changes in fluorescence spectra as a function of water content in aqueous THF solution. $[1] = 5.0 \times 10^{-5}$ M, $\lambda_{\text{ex}} = 340$ nm. Inset shows the profile for the fluorescence intensity at 434 nm as a function of water content.

dioxane.

On the other hand, in THF, compound **1** revealed somewhat blue shifted emission bands with fine structures compared with acetonitrile and dioxane: emission bands were observed around 410, 434, 458, and 495 nm. As shown in Figure 2, addition of water to this solution again resulted in a prominent quenching without significantly affecting the profile of the emission spectra. In this case, about 87% of the total changes in fluorescence intensity were induced by the addition of 1% water, and further increases in water composition resulted in relatively constant emission intensities.

Similar experiments were also performed to assess the possibility of compound **1** as a probe for water contents in methanol-water binary mixture. In methanol solution, very weak fluorescence emissions were observed possibly due to the formation of strong hydrogen bond of compound **1** with the methanol molecules. Addition of water in this solution also affects the fluorescence intensity of **1**, however, the responses were not so useful for the monitoring of water contents due to the very weak and noisy signals compared to the results obtained with other aprotic solvent systems.

The significant spectral changes with a small variation in the composition of solvent mixture usually indicate specific solvent effects.¹⁶ The mechanism of the fluorescence quenching of **1** is believed to be due to the specific interaction of **1** with water molecules, particularly, with the hydroxyl group oxygen and nitrogen atoms of the heterocycles of the compound **1**. The poor fluorescence emission of 8-HQ has been shown to result from a photoinduced tautomerization followed by deexcitation of the tautomer which occurs mainly by a nonradiative route.^{12b} In the presence of water, the tautomerization process might be assisted by the intermolecular proton transfer between each of the two functions (-OH and quinoline nitrogen atom) and surrounding water molecules.

The fluorescence quenching due to the presence of small amount of water in organic solvents can be described by the

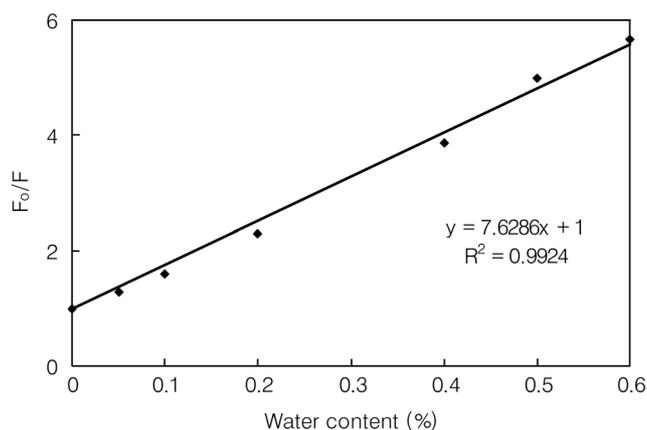


Figure 3. Stern-Volmer plot for the changes in fluorescence intensity of **1** at 463 nm as a function of water content in aqueous acetonitrile solution. $[1] = 5.0 \times 10^{-5}$ M.

Table 1. The Stern-Volmer K values and detection limits for the fluorescent signaling of water content in organic solvents^a

	K (M^{-1})	R^2	Detection limit	
			H_2O (M)	H_2O (%)
Acetonitrile	7.63	0.992	0.0063	0.0113
Dioxane	5.46	0.996	0.0296	0.0534
THF	10.38	0.999	0.0035	0.0062

^a $[1] = 5.0 \times 10^{-5}$ M.

Stern-Volmer equation ($F_0/F = 1 + K[H_2O]$).¹⁷ In the present case, a simple linear relationship between F_0/F (F_0 and F represent the fluorescence intensity in the absence and the presence of water, respectively) and $[H_2O]$ was observed for water contents of lower than 1% (Figure 3) as has been reported earlier work.¹⁷ Among the tested solvents, the highest sensitivity was observed for THF ($K = 10.38 M^{-1}$, Table 1). Detection limits were found to be in between 0.006% (THF) and 0.05% (dioxane) that imply the fact that the compound may be utilized as a chemosensor for the determination of water composition in polar organic solvents commonly used in many chemical laboratory processes.

In summary, a simple 8-hydroxyquinoline based benzoxazole derivative was synthesized and its chemosensing behaviors for the probing of water content in polar organic solvents were investigated. The fluorescence was effectively quenched with small changes in water content by the specific solvent effects with water molecules. The results obtained suggest that the compound **1** may be used as a sensitive fluorescent molecular probe for the assaying of water content particularly in solutions having less than 1% water in aprotic polar organic solvents.

Experimental Section

General. 8-Hydroxyquinoline-2-carboxylic acid and 2-aminophenol were purchased from Fluka Chemical Co. 1H and ^{13}C NMR spectra were measured on a Varian Gemini-2000 spectrometer. HRMS spectra were obtained with a

Micromass Autospec Mass Spectrometer. Fluorescence measurements were performed using an Aminco-Bowman Series 2 Spectrometer. The Karl Fischer measurements were carried out with a Karl-Fischer Moisture Titrator MKS-500 (Kyoto Electronics). All solvents used for spectroscopic measurements were purchased from Aldrich Chemical Co. as 'anhydrous' grade having water content less than 0.001%, 0.003%, and 0.002%, for acetonitrile, 1,4-dioxane, and THF, respectively.

Synthesis of 1. A mixture of 8-hydroxyquinoline-2-carboxylic acid (1 mmol, 0.1 g) and 2-aminophenol (1.2 mmol, 0.07 g) in polyphosphoric acid (2 g) was heated at 150 °C for 24 h under N₂ atmosphere. The reaction mixture was allowed to cool to room temperature and small amount of ice-water was added and the resulting solution was stirred for 2 h. Precipitate was filtered and dissolved in dichloromethane. The solution was filtered and the filtrate was evaporated to dryness. The product was crystallized from CH₂Cl₂/hexane to yield yellow crystals of **1**. Yield 64%, ¹H NMR (300 MHz, CDCl₃) δ 8.46 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.48 (m, 3H), 7.29 (d, *J* = 6 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 153.2, 137.6, 129.9, 129.3, 126.7, 125.4, 121.1, 118.1, 111.5. HRMS (EI+), Calcd for C₁₆H₁₀N₂O₂ 262.0742, Found 262.0742.

Fluorescence Measurements. All the solvents used were commercially available anhydrous grade. Incremental amount of water was added to the stock solution of **1** in organic solvents by a microsyringe or micropipette. After this, the solution was diluted with organic solvents to make the required probe concentration (5.0×10^{-5} M) as well as the water contents in between 0 and 50%. The water contents of the representative analyte solutions were determined by the Karl Fischer method.

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