

A New Chromogenic Water Sensing System Utilizing Deprotonation and Protonation of Anion Receptor

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A simple chromogenic system based on **1**-fluoride was developed to determine water content in organic solvent. This system utilized deprotonation and protonation of the anion receptor **1**. The water content evaluated from this system gave close value to the real water content in the range of 0 to 0.35% in acetonitrile and 0.2 to 0.5% in DMSO. Therefore, protonation and deprotonation phenomenon from the anion receptor by basic anion could be promising method for water sensing system.

Key Words : Deprotonation, Water content in organic solvent

Introduction

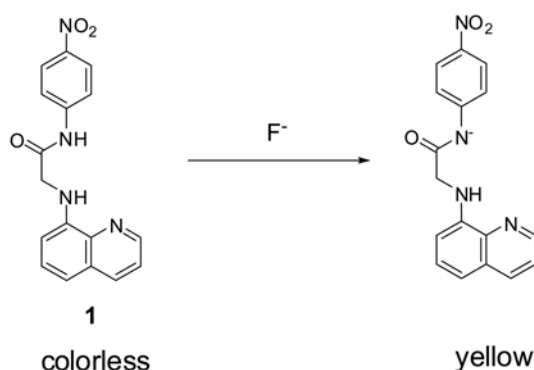
As water is the most common impurity in organic solvents, determination and control of water contents in organic solvents or chemical products are highly important in laboratory chemistry and industrial processes.¹ Karl Fischer titration² and gas chromatography³ have been traditionally used for the determination of water contents. However, these methods have limitations such as requirement for skilled personnel, specialized equipment and incapability of performing continuous monitoring. To overcome these disadvantages, there is increasing interest in optical water sensing system utilizing dye molecules. In this case, dye molecules convert a chemical interaction or recognition process into an optically detectable signal. Optical signaling is simple and convenient compared to the traditional method. In addition, optical signaling is possible to use in situ monitoring and even allows naked eye detection. Various dye molecules have been utilized for this purpose.⁴ Another optical water sensing system utilizes dye-anion complex. Recently Chang *et al.* successfully demonstrated that dye-anion complex could be excellent probe system for the signaling of water in organic solvents.⁵ He utilized the disruptive effect of water on complexation of dyes with anions. In his system, water destroyed hydrogen bonds between dye and anion. In many optical sensing receptors for anions, deprotonation from the receptor has been utilized. On deprotonation, a substantial delocalization of negative charge usually leads to a large red shift, which results in drastic color changes of solution. In consequence, naked detection of the anion becomes possible.⁶ Therefore, we envisioned that reprotonation of the deprotonated receptor could be another good method for water sensing system.

Previously, we reported anion receptor **1**, which has quinoline and nitrophenyl group as signaling groups and amide and amine groups as binding groups.⁷ Receptor **1** proved to be an efficient naked eye detector for fluoride in acetonitrile as deprotonation by fluoride induced typical red

shift with color change. The color of solution changes from colorless to yellow in the presence of fluoride.

The effect of deprotonation is maximized in anhydrous organic solvent since water would interrupt deprotonation from receptor **1**. Therefore, investigation of change from deprotonated **1** to **1** could be another convenient signaling system to determine the water content of organic solvent. From the experiments, the variation of water content was easily noticed through naked eye detectable color changes and the amount of water content in organic solvent was measured by ratiometry in precision.

Receptor **1** displayed strong absorption bands at 320 nm in acetonitrile. Figure 1 shows the family of spectra obtained over the course of the titration of solution **1** with tetrabutylammonium fluoride in anhydrous acetonitrile. As fluoride ions were added to the 40 μ M solution of **1**, λ_{max} of **1** moved from 320 nm to 431 nm due to deprotonation and spectra showed the clear isosbestic point at 356 nm. The presence of the sharp isosbestic point for this system indicates that only two species were present at equilibrium over the course of the titration experiment. When 80-100 equivalents of fluoride were added, changes of spectra were not observed, which indicated most of amide N-H proton is deprotonated. Therefore, we added 100, 150, 200 and 500 equivalents of fluoride to **1** to eliminate uncertainty intro-



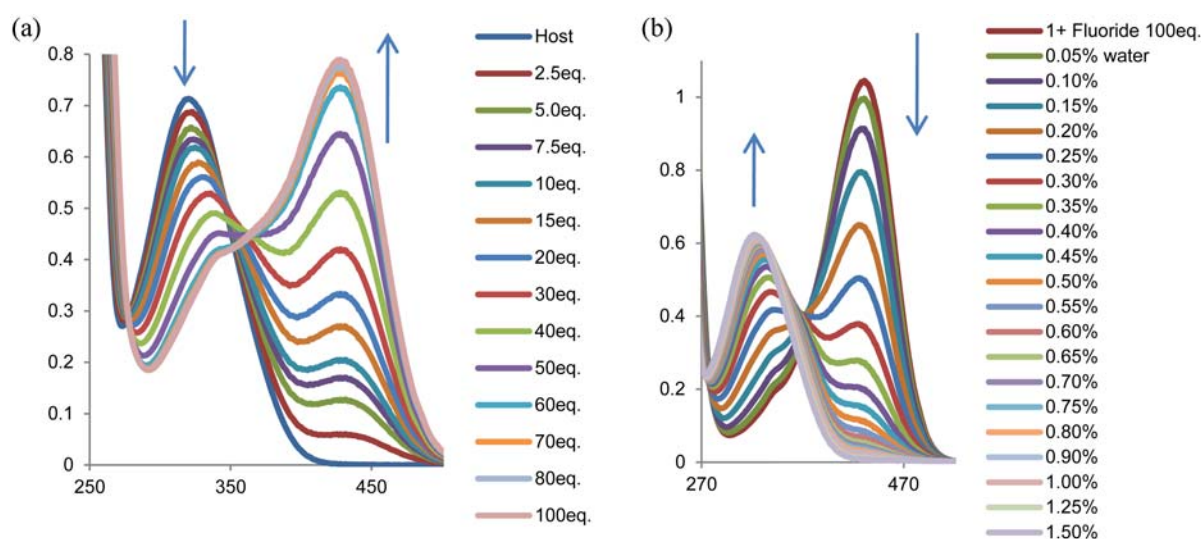


Figure 1. Changes of UV-vis spectra of **1** in the presence of varying amounts of fluoride in 40 μ M anhydrous acetonitrile solution (a) and changes in the UV-vis spectra of the **1**-F system as a function of water content in acetonitrile (b).

duced by using exact amount of fluoride. As water was added to the deprotonated **1** (**1** and 100-200 equivalents of fluoride) in anhydrous acetonitrile, λ_{max} moved from 431 nm to 320 nm and finally spectrum turned into that of **1** alone. At the same time, the color of solution gradually turned from yellow to colorless. This change was due to regeneration of **1** through the protonation of deprotonated **1** by water molecules. This result suggests that **1**-fluoride system could be used as an optical probe for water content in organic solvents.

Therefore, we investigated the systematic signaling of water content in acetonitrile with **1**-fluoride system. The change of UV spectrum as a function of water content in acetonitrile was measured (Figure 1(b)). As the water content increased, the spectrum gradually converted from the spectrum of **1**-fluoride to that of **1** only. The changes in the absorption spectrum of **1**-fluoride system as a function of water content analyzed following Chang's ratiometry using

the ratio of two absorbances at 431 nm and 320 nm.⁵ A_{431}/A_{320} as a function of water content was plotted to obtain a correlated relationship (Figure 2). In this plot, while **1** and 100-200 equivalents of fluoride gave similar correlationship according to the water content, **1** and 500 equivalents of fluoride system gave much insensitive response toward changes in the water content. Probably when the concentration of fluoride is too high, fluoride might react with H_2O , which cause error in estimation of the amount of H_2O . Therefore we used only 100-200 equivalents of fluoride.

In DMSO similar phenomenon was observed (Figure 3). In the case of DMSO, water content analyzed using the ratio of two absorbances at 446 nm and 335 nm (Figure 4). Plotting showed good correlationship in the low water content region. In the case of acetonitrile, the changes were prominent in the range from 0 to 0.35%. In the case of DMSO, the changes were prominent in the range from 0.2 to 0.5%. Therefore, a calibration curve for the determination of water content could be drawn in this range. From the

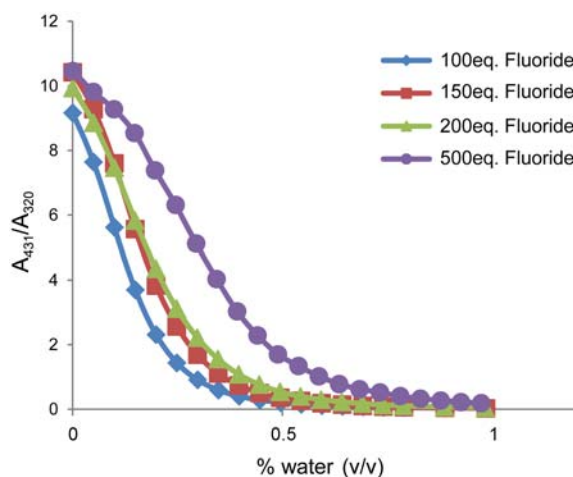


Figure 2. Changes in A_{431}/A_{320} as a function of % water and effect of fluoride concentration on UV titration of **1**-fluoride system with water in acetonitrile.

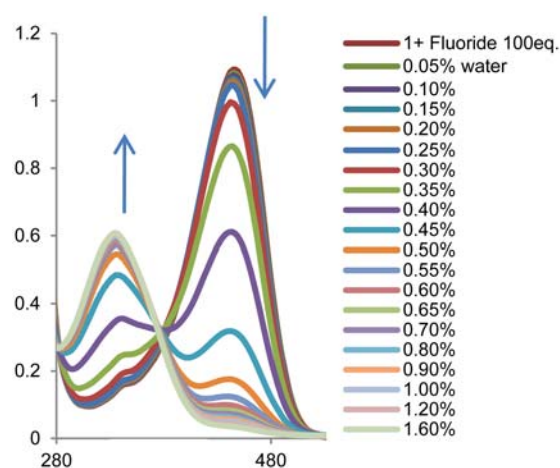


Figure 3. Changes in the UV-vis spectra of the **1**-F (100 equivalents) system as a function of water content in DMSO.

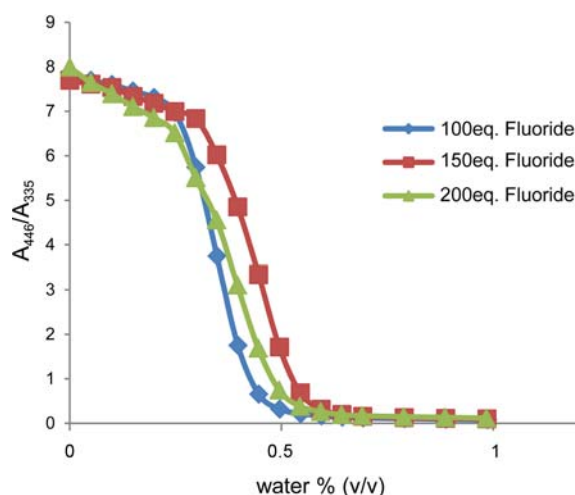


Figure 4. Changes in A_{446}/A_{335} as a function of % water and effect of fluoride concentration on UV titration of **1**-fluoride system with water in DMSO.

Table 1. The accuracy test of **1**-fluoride system for the determination of water content in acetonitrile and DMSO

F^-	Acetonitrile		DMSO	
	R^2	0.1% water	R^2	0.35% water
100eq.	0.9994	0.096	0.9901	0.362
150eq.	0.9973	0.091	0.9939	0.382
200eq.	0.9982	0.106	0.9953	0.368

plotting, it turned out that increased amount of fluoride resulted in less sensitive response toward changes in the water content. However, the equivalents of fluoride did not affect much for the determination of water content in the 100- 200 equivalents of fluoride region (Table 1).

To verify efficiency and accuracy of **1**-fluoride system, we tested the system to the organic solvent with known water content. The values obtained from acetonitrile were more accurate than the value obtained from DMSO.

In summary, a simple chromogenic system based on **1**-fluoride was developed to determine water content in organic solvent. This system utilized deprotonation and protonation of receptor **1**. The water content evaluated from this system gave close value to the real water content in the range of 0 to

0.35% in acetonitrile and 0.2 to 0.5% in DMSO. Therefore, protonation and deprotonation phenomenon from the anion receptor by basic anion could be promising method for water sensing system.

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