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4, 4'-Diamino-4"-methoxytriphenylamine as highly sensitive fluorimetric sensor for the determination of water in organic solvents

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Abstract

In this work, we report fast and low-cost fluorimetric system for the determination of trace amounts of water in both aprotic and protic organic solvents. The analytical signal of the proposed method is based on the quenching effects of water on the fluorescence emission spectrum of (4, 4'-diamino-4"-methoxytriphenylamine) molecule. It was found that physical interactions such as hydrogen bonding are responsible for the observed quenching effect. The limit of detection values for the determination of water in DMSO, acetonitrile, ethanol and methanol were 0.0727, 0.0636, 0.0761 and 0.0631 (W/W%), respectively. The limit of quantitation values in DMSO, acetonitrile, ethanol and methanol were 0.2734, 0.2546, 0.2540 and 0.2531 (W/W%), respectively. Simplicity, low cost and high speed of the proposed water sensing system make it a valuable candidate to be used in industrial applications such as quality control procedures. In addition, it can be used for the determination of water in redox active solvents such as DMSO, where the standard Karl Fischer method gives problematic results.

Keywords 4, 4'-Diamino-4"-methoxytriphenylamine · Ethanol · Methanol · DMSO · Water determination · Fluorescence

Introduction

Water as one of the impurities in the organic solvents can damage different laboratory instruments and interfere in the industrial processes such as pharmaceutical and petrochemical production lines, food processing, paper production and fine chemical industry [1]. Therefore, determination of trace amounts of water in the organic solvents is an important research area. Classic and widely used technique for water determination in organic solvents is Karl Fischer method [2]. Although this method has several advantages including sensitivity and accuracy, some limitations such as use of toxic and expensive reagents, use of substantial amount of sample, slow reaction rate, requirement for skilled personnel and possible interferences from redox active spices have restricted its application. To date, several methods such as chromatography [3], IR spectroscopy [4], potentiometry [5], Raman spectroscopy [6], solid-phase extraction [7], holographic method [8], absorbance-based film sensors [9], impedance-based electrochemical methods [10],

Kiomars Zargoosh Kiomarszargoosh@cc.iut.ac.ir conductometry [11] and amperometry [12] have been used for the determination of water in organic solvents. Most of these methods suffer from disadvantages like complexity in operation and cost of used materials. In addition, some of them cannot be used for the determination of water in redox active solvents such as dimethyl sulfoxide (DMSO).

Nowadays, with the advancement of optical technology, fluorescence sensors have received a considerable attention for their applications in the determination of water contents of organic solvents. They are easy to fabricate and applicable in the remote and in situ monitoring. An ideal fluorescencebased sensor for water must exhibit high quantum yield and strong changes in its fluorescence intensity upon interacting chemically or physically with the water molecules. In recent years, many efforts have been made to achieve fluorescence sensors for the determination of water in different organic solvents [13].

In this paper, we report the fluorimetric method for the determination of low amounts of water in different organic solvents such as dimethyl sulfoxide (DMSO), acetonitrile (MeCN), ethanol and methanol using the quenching effect of water on the fluorescence intensity of the (4, 4'-diamino-4"-methoxytriphenylamine) (DAP) molecules. The proposed system exhibits significant advantages including high sensitivity, rapid response, low-cost procedure and simplicity

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in synthesis and application of the DAP sensing molecules. In addition, the proposed sensor is able to determine water in dimethyl sulfoxide (DMSO), where Karl Fischer method cannot be used.

Water can influence the intensity and wavelength range of the fluorescence spectra of the fluorimetric sensors through different mechanisms such as complexation, decomposition, hydrogen bonding, dipole–dipole interaction and additional reactions [13]. In this work, the mechanism of the water quenching effect on the fluorescence intensity of the DAP was carefully discussed and it was found that the hydrogen bonding between DAP sensing molecule and water is responsible for observed quenching effect.

Experimental

Chemicals and reagents

Analytical-grade dimethylsulfoxide (DMSO), quinine sulfate, acetonitrile, methanol, sodium, phosphorus pentoxide (P₂O₅), magnesium and iodine were purchased from Merck (Germany). Cesium fluoride (99%), *p*-anisidine (97%), Pd/C (10%) and 1-fluoro-4-nitrobenzene (99%) were purchased from Sigma-Aldrich. Absolute ethanol was purchased from Bidestan (Iran). Hydrazine hydrate (85%) was obtained from Merck. Double-distilled water was used throughout. The concentrations of DAP solutions used for absorption and fluorescence measurements were in the order of 1×10^{-7} -5×10^{-5} M. The concentration of the quinine sulfate standard solution used for calculating the fluorescence quantum yield of DAP was 1×10^{-6} M. The quinine sulfate standard solution was prepared in the 0.1 M H₂SO₄.

Apparatus

FT-IR spectra were recorded by a Jasco-680 FT-IR spectrophotometer (Japan) with KBr pellets. ¹H-NMR spectra of monomers in deuterated DMSO were recorded using Bruker Avance 400 MHz spectrometer. All chemical shifts are reported in ppm. Jasco-FP-570 UV–visible spectrophotometer (Japan) was used for recording the absorption spectra. All fluorescence measurements were taken using a Shimadzu RF-5301PC fluorescence spectrophotometer (Japan) using 1-cm quartz cell. Elemental analysis was performed with a LECO CHNS-932 (USA).

Drying the organic solvents

The previously established methods were applied for removing the trace moisture from organic solvents [14]. For drying acetonitrile, 50 mL of it was poured in the round-bottomed flask; then, 0.5 g of P_2O_5 was added to the solvent and refluxed for 12 h. Then, the solution was distilled. The remaining solid particles were separated by filtering, and the obtained dry acetonitrile was stored in the sealed glass.

A repeated freezing-out method was used for drying DMSO. Briefly, a beaker containing 150 mL of DMSO was immersed in a water bath at temperature of 10 °C. At this temperature, DMSO begins to freeze. Before complete freezing, the trace amount of water together with small volume of DMSO remains as liquid. Then, the solid portion of DMSO was separated and heated to a temperature of 30 °C. After complete melting of solid DMSO, again the beaker containing the melted DMSO was placed in the water bath at 10 °C. This procedure was repeated 5 times to insure complete removal of trace amount of water that may be present in the analytical-grade DMSO.

For drying methanol, the magnesium was contacted with 200 mL of methanol for 6 h at room temperature. Then, 2 g of sodium and 20 mg of iodine were added to the methanol and refluxed for 2 h. Then, the waterless methanol was separated by distillation and stored in the sealed glass flask.

Sodium was contacted with ethanol to remove trace amounts of water from it. In typical experiment, 2 g of sodium was added to 120 mL of ethanol and refluxed for 1 h. Then, the ethanol was distillation and stored in the sealed glass vessels.

Recording the absorbance and fluorescence spectra

The DAP solutions in the concentration range of 1.0×10^{-7} - 5.0×10^{-5} M in each solvent were used for recording the absorbance, fluorescence emission and fluorescence excitation spectra in the wavelength range of 200–700 nm.

To study the quenching effects of water on the fluorescence emission spectra of DAP, 2 mL aliquots of the solutions containing predefined concentration of DAP was poured in the 1-cm quartz cell. Then, using a microsyringe, different volumes of water were added to the solutions and properly mixed before recording the spectra. Then, the fluorescence emission spectrum of each solution was recorded and corrected for dilution effects due to the addition of water. Water causes quenching effect on the fluorescence emission spectra of the DAP solutions in all solvents. The reduction in the fluorescence intensity at the λ_{max} of the spectra was regarded as analytical signal.

Similar experimental conditions were applied for recording the UV–Vis absorbance spectra of the DAP in different organic solvents.

Synthesis of 4, 4'-dinitro-4"-methoxytriphenylami ne (DNP)

Previously reported method was used for the synthesis of 4, 4'-dinitro-4"-methoxytriphenylamine (DNP) [15]. The graphical representation of this synthesis is depicted in Scheme 1. Briefly, in a 50-mL two-necked round-bottomed flask, 1.52 g of cesium fluoride was stirred in 10 mL of DMSO at room temperature. Then, 1.17 g (8.2 mmol) of 4-fluoronitrobenzene and 0.5 g (4 mmol) of *p*-anisidine were added to the mixture. The mixture was stirred at 120 °C for 24 h. The mixture was poured into 40 mL of methanol and stirred for 5 min. The precipitated orange-red powder was collected by filtration and washed several times with methanol-water (1:1). The mass of the obtained orange-red DNP powder was 1.31 g. MP: 210-213 °C; FT-IR (KBr): $\nu = 3075$ (CH sp², w), 2916 (CH sp³, w), 1576 (C=C_{arom}, *m*), 1576 (NO₂, *s*), 1469 (C=C_{arom}, *m*), 1339 (NO₂, *s*), 1278 (s), 1110 (s) cm⁻¹; ¹H-NMR (DMSO- d_6 , ppm): 8.24 (d, 4H, Aromatic), 7.33 (*d*, 4H, Aromatic), 7.25 (*d*, 4H, Aromatic), 7.14 (d, 2H, Aromatic), 3.76 (s, 3H, CH₃). Elem. Anal. Calcd. for C₁₉H₁₅N₃O₅: C, 62.46%; H, 4.14; %; N, 11.50%. Found: C, 62.27%; H, 4.21%; N, 11.53%.

Synthesis of 4, 4'-diamino-4"-methoxytriphenylami ne (DAP)

Previously reported method was used for the synthesis of 4, 4'-diamino-4"-methoxytriphenylamine (DAP) [15]. The DAP synthesis steps have been depicted in Scheme 2. For synthesis of DAP, 0.73 g (2 mmol) of DNP was dissolved in

15 mL ethanol in a 50-mL three-necked flask. Then, 0.015 g of 10% Pd/C was added to the obtained solution. The mixture was stirred at 60 °C, and 1 mL of hydrazine hydrate was added slowly to it. Then the solution was stirred at 85 °C for 15 h under N₂ atmosphere. After that, a clear solution was obtained by filtration and removal of Pd/C. Finally, the solution was cooled to precipitate the solid product. The precipitates were collected by filtration, washed with cold ethanol and dried in vacuum at 80 °C. The mass of the obtained light green DAP needles was 0.49 g. MP: 149-152 °C; FT-IR (KBr): 3451, 3412 (N–H stretch, NH₂, m), 3036 (CH sp², w), 2928 (CH sp³, w), 1625 (C=C_{arom}, m), 1502 (C=C_{arom}, s), 1265 (s), 829 (m) cm⁻¹; ¹H-NMR (DMSO-*d*₆, *d*, ppm): 6.79 (d, 2H, Aromatic), 6.73 (6H, Aromatic), 6.53 (d, 4H, Aromatic), 4.81 (4H, NH₂), 3.65 (s, 3H, CH₃). Elem. Anal. Calcd. For C₁₉H₁₉N₃O: C, 74.73%; H, 6.27%; N, 13.76%. Found: C, 76.56%; H, 6.32%; N, 13.89%.

Results and discussion

Characterization of DNP and DAP compounds

FT-IR spectra of DNP and DAP are depicted in Fig. 1. In Fig. 1a, two absorption bands at around 1576 cm⁻¹ and 1339 cm⁻¹ are related to nitro groups. In the FT-IR spectrum (b) of DAP, the removal of the absorption bonds at 1576 cm⁻¹ and 1339 cm⁻¹ and appearance of absorption bonds at 3412 cm⁻¹ and 3451 cm⁻¹ confirm the synthesis of the diamine (DAP) compound from dinitro compound (DNP). Due to chemical composition similarity of DNP





4000 3600 3200 2800 2400 2000 1600 1200 800 400 Wavenumber (cm⁻¹)





Fig. 2 1 H-NMR spectra of DNP (a) and DAP (b) compounds in deuterated DMSO

Fig.1 FT-IR spectra of the synthesized compounds: DNP (\boldsymbol{a}) and DAP (\boldsymbol{b})

and DAP, other defined absorption bonds in Fig. 1 are same in the spectrum (a) and spectrum (b). As shown in Fig. 1, these bonds clearly are in agreement with the proposed chemical structure for DNP and DAP synthesized compounds.

The ¹H-NMR spectra of DNP and DAP are shown in Fig. 2. As shown in Fig. 2 and represented in "Experimental" section, the position and intensity of all proton peaks are in complete agreement with the proposed molecular structure of DNP and DAP.

The elemental analysis of DNP and DAP was performed to confirm the success of synthesis reactions. The calculated mass percent values for DNP ($C_{19}H_{15}N_3O_5$) are: C, 62.46%; H, 4.14; %; N, 11.50.

The found values from elemental analysis are C, 62.27%; H, 4.21%; N, 11.53%. The nice agreement between calculated and found values confirms the proposed formula for DNP. Also, the calculated mass percent values for DAP ($C_{19}H_{19}N_3O$) were: C, 74.73%; H, 6.27%; N, 13.76%. The empirical values were: C, 76.56%; H, 6.32%; N, 13.89%. As is clear from these results, there is high level of consistency between empirical and calculated values confirming the proposed chemical formula for DAP.

Spectral characteristics of DAP in different organic solvents

Our primary experiments showed that diluted solutions of DAP in dry organic solvents exhibit intense fluorescence when excited with photons in the wavelength range lower than 400 nm. Figure 3 shows the fluorescence excitation and emission spectra of DAP $(3.3 \times 10^{-6} \text{ M})$ in different organic solvents. It seems that conjugation between the aromatic rings and nitrogen atoms in DAP is responsible



Fig. 3 Excitation spectra of 3.3×10^{-6} M solution of DAP in DMSO (a), MeCN (b), EtOH (c), MeOH (d) and emission spectra of DAP in DMSO (e), MeCN (f), EtOH (g) and MeOH (h)

for the π - π * transition and thus the development of fluorescence. As shown in Fig. 3, excitation and emission spectra of DAP in protic solvents (MeOH and EtOH) occurs at shorter wavelength range. This is due to the formation of hydrogen bonding between protic solvent molecules and DAP. Protic solvents can form hydrogen bonds with DAP molecules in both ground- and excited-state energy levels. It seems that MeOH and EtOH form stronger hydrogen bonds with DAP molecules in the ground state.

As the result, the ground-state energy level in DAP becomes more stabilized than excited-state energy level, and hence, the energy gap between ground and excited states is increased and the resulted blueshift is observed. Similar observation has been reported for different fluorescent molecules in protic solvents [16].

In addition, DAP exhibited stronger emissions in polar aprotic solvents (acetonitrile and DMSO) than those in polar protic solvents (methanol and ethanol). In general, fluorescence is quenched in protic solvents with stronger hydrogen donor ability [17]. Also, the fluorescence can be quenched due to the formation of hydrogen bonding. Hydrogen bonding can reduce the π -electron freedom and hence reduce the strength of the conjugation cycle in the molecular orbital and hence decrease the fluorescence intensity. In addition, hydrogen bonding can enhance the possibility of the occurrence of the photoinduced electron transfer (PET) process. PET between the solute and solvent can occur by passing through the excited-state strengthened intermolecular hydrogen bonding. After the formation of the hydrogen bonds, the electronic coupling between solute and solvent molecules is enhanced and PET is clearly simplified by the excited-state strengthened intermolecular hydrogen bonds [16, 17].

To make more quantitative comparison between fluorescence intensity of DAP in different organic solvents, the fluorescence quantum yield φ_F of it was measured using quinine sulfate standard method [18]. The quinine sulfate standard solution ($\varphi_F = 0.58$) was prepared in 0.1 M H₂SO₄. The fluorescence quantum yield of DAP was calculated using Eq. 1 [18]:

$$\varphi_{\rm F(sample)} = \varphi_{\rm F(Ref)} (I_{\rm sample} / A_{\rm sample}) (A_{\rm Ref} / I_{\rm Ref}) (n_{\rm sample} / n_{\rm Ref})^2$$
(1)

where I is the integrated fluorescence intensity; A, the absorbance; and n, the refractive index of solvent used.

The obtained fluorescence quantum yields together with excitation and emission wavelength in different organic solvents are summarized in Table 1. As given in Table 1, DAP has higher fluorescence quantum yields in aprotic solvents. Theoretically, H bonding of MeOH and EtOH with DAP can be taken place via oxygen atom of alcohols and amine protons of DAP or nitrogen atom of amine

Table 1 Fluorescence quantum yield $\varphi_{\rm F}$ values of DAP in DMSO, MeCN, EtOH and MeOH

	Excitation wavelength λ_{ex} (nm)	Emission wavelength $\lambda_{\rm em}$ (nm)	$\varphi_{\rm F}(\%)$
DMSO	326	453	24
MeCN	320	434	12
EtOH	313	429	7
MeOH	305	426	1.3

groups of DAP and hydroxyl protons of alcohols. It seems that the latter is responsible for the observed reduction in the fluorescence quantum yields of DAP in protic solvents. Thus, the formation of H bonding of amine protons of DAP with water molecules has been confirmed using ¹HNMR study in the next section.

Mechanism of the water quenching effect on the DAP fluorescence

Our primary experiments revealed that the addition of water to the diluted solution of DAP in dry organic solvents imposes notable quenching effect on the fluorescence intensity of the DAP solution. Figure 4 shows the quenching effect of water on the fluorescence intensity of DAP in different organic solvents. As shown in Fig. 4, the fluorescence intensity of DAP continuously decreases with the increase in the water contents of the DAP solution. Although water causes the significant quenching effect on the fluorescence intensity of DAP solution, it does not cause any change in the spectral feature of the DAP solution in all studied organic solvents. For example, by the addition of water to the DAP solution no change was observed in the maximum emission wavelength (λ_{max}) of the DAP solution in all studied solvents. This observation indicates that water does not change the energy gap between ground state and excited state responsible for the fluorescence emission in the DAP molecule. This result is in agreement with physical quenching mechanism, in which water creates new non-radiation relaxation routes to dissipate the excess energy of the DAP excited molecules.

This physical quenching effect can arise from hydrogen bonding interactions between amine groups of DAP and water, interrupting the conjugation of the π -electrons in DAP aromatic ring and hence reducing the possibility of radiation relaxation of the excited DAP molecules [19].

For more clarification on the mechanism of the quenching effect of water on the fluorescence intensity of DAP, the absorbance spectra of DAP in different organic solvents and in the presence of different concentrations of water were recorded. Figure 5 shows the typical absorbance spectra of DAP in MeCN and in the presence of water concentration







Fig. 5 Absorption spectra of 3.7×10^{-5} M DAP solution in MeCN in the presence of different V/V% of water

ranging from 0 to 4.76 V/V%. The spectra were corrected for dilution effect of water. As shown in Fig. 5, water only decreases the absorbance intensity of DAP solution in MeCN and spectral characteristics of DAP remained intact. Similar absorbance spectra were observed for DAP solution in other tested organic solvents. Again, constancy of the absorbance spectral characteristics of DAP solution in the presence of water confirmed that observed quenching effect origins from physical interactions such as hydrogen bonding. The band gap for the excitation of the H₂O molecule to its lowest excitation state is about 7 eV [20]; thus, it cannot be directly excited by the light with the wavelength range of 300-320 nm that was used in this work for the excitation of DAP. Although the formation of hydrogen bonds between DAP and H₂O can lower the required energy for exciting the H₂O molecules, this effect is rarely acceptable to be enough for lowering the band gap of water molecules to be excited with 300–320 nm photons. Thus, the possible mechanism for this quenching effect can be formulated as the following equations:

$$DAP + hv \to [DAP]^* \tag{2}$$

$$[DAP]^* + H_2O \rightarrow [DAP \dots H_2O]^*$$
(3)

$$[\text{DAP} \dots \text{H}_2\text{O}]^* \rightarrow [\text{DAP} \dots \text{H}_2\text{O}] + \text{heat}$$
 (4)

$$|\text{DAP} \dots \text{H}_2\text{O}| \rightarrow \text{DAP} + \text{H}_2\text{O}$$
 (5)

Based on this mechanism, the formation of the hydrogen bonds between water and DAP* can open the non-radiation relaxation routes for the dissipation of the excess energy of the [DAP... H_2O]*, hence imposing the resulted quenching effect.

Another experiment that confirmed the physical nature of the water quenching effect had recorded the florescence emission spectra of DAP solutions in the presence of constant concentration of water in the different organic solvent at the heating–cooling temperature cycle. Figure 6 shows the fluorescence intensity 3.7×10^{-5} M solution of DAP in DMSO and in the presence of 2.67 W/W% of water. In Fig. 6, graph (a) shows the fluorescence intensity of DAP solution during heating cycle from 20 to 40 °C and graph (b) shows the fluorescence intensity of the heated DAP solution during cooling period from 40 to 20 °C. As shown in Fig. 6a, the fluorescence intensity of DAP



solution decreases when temperature increases from 20 to 40 °C. This observation is common phenomenon for fluorescence spectra, because at higher temperature the collision between solute and solvent molecules occurred at higher speeds that results in the non-radiation relaxation of the excited solute molecules.

Figure 6b shows that fluorescence intensity of the preheated solution increases when its temperature cooled from 40 to 20 °C. Complete reversibility of the fluorescence intensity confirms that no covalent band formed between water and DAP molecules. If covalent band formation occurred, the chemical structure of DAP would change, and hence, complete reversibility of the fluorescence intensity was not possible.

Constancy of the spectral characteristics of the fluorescence spectra of DAP in the presence of different amounts of water is notable advantage where the method is applied for quantitative determination of water in organic solvents,

because λ_{max} does not change and all measurements can be taken at same wavelength.

For more clarification of the quenching mechanism, the ¹H-NMR spectra of DAP in the pure DMSO- d_6 and in DMSO- d_6 after the addition of 5 W/W percent of D₂O were recorded. The obtained spectra are depicted in Fig. 7. As shown in Fig. 7, after the addition of D_2O the peaks of the NH₂ protons at about 4.8 ppm have been almost disappeared from the spectrum. This observation indicates that the interaction between DAP and water is taken place via hydrogen bonding of amine protons of DAP and oxygen atom of water molecules.

Calibration curves for the determination of water in organic solvents

The quenching effect of water on the fluorescence intensity of the DAP was used for the determination of water in the



in deuterated DMSO including of 5% of D₂O

organic solvent. To obtain the best calibration curves, the intensity–concentration data were fitted to different equations. It was found that Stern–Volmer equation [2] gives the best linear relation between water content and fluorescence intensity. The Stern–Volmer equation can suitably describe the intensity–concentration as Eq. 6:

$$F_0/F = 1 + K_{\rm SV}[Q] \tag{6}$$

where F_0 and F are the fluorescence intensities in the absence and presence of water, respectively. K_{SV} is the S–V quenching constant, and [Q] is the quencher (water) concentration. The obtained linear equation, linear range and related R^2 values are given in Table 2.

In addition, the Stern–Volmer plots of F_0/F versus [H₂O] in different organic solvents are shown in Fig. 8. As shown in Table 2 and Fig. 8, there is a nice linear relation between water content of organic solvent and F_0/F ratio.

The limit of detection (LOD) of the method for the determination of water in each solvent was calculated using Eq. 7:

$$LOD = 3\delta/m \tag{7}$$

Table 2 Linear equation, linear range and related R^2 values for the determination of water in different organic solvents

Solvent	Linear equation	Linear range (V/V%)	R^2 value
DMSO	$F_0/F = 0.0792 [H_2O] + 0.955$	0.244–5	0.9821
MeCN	$F_0/F = 0.1053 [H_2O] + 0.9494$	0.205-5	0.9842
EtOH	$F_0/F = 0.181 [H_2O] + 0.9761$	0.202–5	0.9975
MeOH	$F_0/F = 0.119 [H_2O] + 1.0096$	0.224-4	0.9908

where δ is the standard deviation of the F_0/F and *m* is the slope of the linear equation in Table 2. In addition, the limit of quantitation (LOQ) of the method for the determination of water the studied organic solvents was calculated using Eq. 8:

$$LOQ = 10 \,\delta/m \tag{8}$$

The calculated LOD (V/V%) and LOQ (V/V%) values are given in Table 3.

In Table 4, the calculated LOD and LOQ values have been compared with those previously reported methods for the determination of water in organic solvents. In Table 4, the calculated LOD and LOQ values have been reported in W/W% to be comparable with the previously reported works in the literature. It can be concluded that our method shows significant advantages over recently reported method for the determination of water in organic solvents. Firstly, our method is fast and complete fluorescence spectrum for each sample can be recorded in less than 1 min. This issue is important for determining water content in large numbers of the organic solvent samples. It must be noted that the overall time needed for performing the titration procedure of the

 Table 3
 Detection limit and limit of quantification of the proposed method for the determination of water in different solvents

Solvent	Detection limit (V/V%)	Limit of quanti- fication (V/V%)
DMSO	0.08	0.3
MeCN	0.05	0.2
EtOH	0.06	0.2
MeOH	0.05	0.2



Detection limit (W/W%)	Quantitation limit (W/W%)	Refs.	Sensing strategy
0.02 (MeCN)	0.07 (MeCN)	[19]	Water-induced interpolymer π -stacking aggregation
0.1 (EtOH)	0.3 (EtOH)		
0.009 (MeCN)	0.026 (MeCN)	[21]	PET
0.009 (EtOH)	0.027 (EtOH)		
0.038 (MeCN)	Not given	[22]	Intramolecular charge transfer (ICT)
0.060 (EtOH)			
0.01 (MeCN)	Not given	[23]	Excited-state intramolecular proton transfer (ESIPT)
0.002 (EtOH)	Not given	[24]	Water as a competitive ligand
0.003(MeCN)	Not given	[25]	Water as a competitive ligand
0.0044 (DMSO)	0.0147 (DMSO)	[26]	Chemical reaction
0.0032 (MeCN)	0.0108 (MeCN)		
0.0026 (MeOH)	0.0085 (MeOH)		
0.0007 (MeCN)	Not given	[27]	Aggregation-based monomer-excimer switching
0.06 (EtOH)			
0.2 (MeOH)			
0.088 (MeCN)	Not given	[28]	Water-induced interpolymer π -stacking aggregation
0.019 (EtOH)			
0.63 (DMSO)	Not given	[29]	Hydrogen bonding interactions
0.26 (MeCN)			
2.1 (MeOH)			
0.008 (MeOH)		[30]	Karl Fischer
0.0064 (THF)	Not given	[31]	
0.0422 (Acetone)			
0.192 (MeCN)			
0.0727 (DMSO)	0.2734 (DMSO)	This work	Hydrogen bonding interactions
0.0636 (MeCN)	0.2546 (MeCN)		
0.0758 (EtOH)	0.2531 (EtOH)		
0.0631 (MeOH)	0.2531 (MeOH)		

 Table 4 Comparison of LOD and LOQ values of the proposed method with those of the recently reported methods for the determination of water in organic solvents

standard Karl Fischer method for the determination of water is higher than 20 min. Secondly, our method is applicable for both protic and aprotic organic solvents. Thirdly, it can be used for the determination of water in redox active solvents such as DMSO, where Karl Fischer standard method cannot be used. Fourthly, the total cost per sample is very low, because 2 mL portion of the low-concentration (about 1×10^{-6} M) solution of DAP is enough for obtaining the fluorescence spectrum of each sample. The total cost of the proposed method is less than 2 USD. The total cost of the Karl Fischer standard method is higher than 8 USD. Based on the above-mentioned results, our method has good potential to be used for quality control of organic solvents in the industrial production line of them.

Interfering effect of ionic species

The solubility of the anionic and cationic species in the organic solvents is limited, and hence, their interfering effect

seems to be negligible. The possible interfering effect of the Na⁺, K⁺, Cl⁻, Ca²⁺, NO₃⁻ ions was studied. Due to solubility limitations, the concentrations of the studied ions in each solvent must be kept less than 5×10^{-6} M. The fluorescence intensities of the 1×10^{-6} M solution of DAP in each solvent and in the absence of the studied ions were recorded. Then, the procedure was repeated in the presence of different concentrations of each ion. The tolerance limit was defined as a concentration of an interfering ion that can cause a 5% deviation in the fluorescence signal of the 1×10^{-6} M solution of DAP. In all cases, the observed deviations were less than 3.2%; thus, the proposed method has notable selectivity for the determination of water in the presence of the ionic species.

Evaluation of the method repeatability

To evaluate the repeatability of the proposed method, the water content of each solvent was repeatedly (n=5) **Table 5**Evaluation of themethod repeatability for thedetermination of water at threedifferent concentrations in thestudied solvents

Solvent	Water content (V/V%)	RSD %
DMSO	0.45	2.1
	2.67	0.9
	5.00	0.8
MeCN	0.25	0.9
	2.67	1.1
	5.00	1.9
EtOH	0.25	2.7
	2.67	2.1
	5.00	1.5
MeOH	0.25	2.7
	1.96	1.6
	3.85	2.2

Table 6 Comparison of the results of the water content (V/V%) determination in the real samples using fluorimetric method and standard Karl Fischer method

Solvent	Karl Fischer	Fluorimetric method
DMSO	No result	0.35 ± 0.03
MeCN	0.32 ± 0.021	0.30 ± 0.02
EtOH	0.41 ± 0.008	0.43 ± 0.03
MeOH	0.53 ± 0.022	0.51 ± 0.03

determined. In each solvent, the water content at three different concentrations was determined. In each solvent, the first concentration was selected near the quantitative limit in the calibration curve (low water content). The second point was selected at the middle of calibration curve, and the third point was selected at the upper end of the calibration curve. The results are given in Table 5. As given in Table 5, the proposed fluorimetric method shows excellent repeatability for the determination of water throughout the dynamic range in all studied solvents.

Real sample analysis

To study the applicability of the proposed method for the determination of water in the real samples of the studied organic solvents, the industrial-grade solvent samples of DMSO, MeOH, EtOH and MeCN were purchased and their water content was determined with the proposed fluorimetric method. Then, other aliquots of the samples were analyzed by standard the Karl Fischer method with coulometric endpoint system. The obtained results are compared in Table 6. As given in Table 6, there is a nice agreement between the results obtained by the proposed fluorimetric method with those of the Karl Fischer method for MeOH, EtOH and

MeCN. In addition, Karl Fischer method was not able to be used for analyzing the water content of the DMSO samples.

Conclusions

The proposed fluorimetric system showed its capability for the determination of water in both protic and aprotic organic solvents. Simplicity, low cost and high speed of the proposed water sensing system make it a valuable candidate to be used in industrial applications such as quality control procedures. In addition, it overcomes the limitation of the standard Karl Fischer method for the determination of water in redox active solvents such as DMSO.

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