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Uncovering the true mechanism of optical detection of HSO_4^- in water by Schiff-base receptors – hydrolysis *vs.* hydrogen bonding†

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The mechanism of optical detection of HSO_4^- in aqueous medium by Schiff-base receptors has previously been proposed to depend on selective hydrogen-bond interactions. Here, we clearly demonstrate for the first time that the acidic nature of this anion gives rise to hydrolysis of the Schiff base, which leads to the optical changes observed in this family of receptors.

The detection and sensing of HSO_4^- ion is of current interest due to its Janus-faced properties in various fields.[1] For this purpose a number of chemoreceptors have been designed, synthesized and evaluated by various workers in last few years.[2–4] Most of them are optical sensors and give fluorimetric/colorimetric responses.[2,3] These receptors can be classified into two classes *viz.*, non-Schiff bases[2] and Schiff bases.[3] The former involve real hydrogen bonding with HSO_4^-. Their tailored design enable them to interact with HSO_4^- as well as a few other tetrahedral analytes such as $HClO_4$, ClO_4^-, $H_2PO_4^-$, SO_4^{2-} *etc.* through hydrogen bonding.[2] One of the major bottle-necks of these receptors is their water intolerance which restricts their use for real sample analysis in aqueous solutions.

However, the Schiff-base type receptors reported by a number of workers in the last four to five years have been quite successful for HSO_4^- detection even in aqueous/semi-aqueous solutions.[3] The mechanism proposed is similar to that for the non-Schiff-base type receptors *i.e.*, hydrogen bonding between the HSO_4^- and the corresponding receptor. As we have also been working in the field of design and synthesis of optical receptors[5] we went through these papers. In this context reports by Kim *et al.* in 2009 involved fluorescent receptors[3a] while all the remaining reports were of colorimetric type.[3b–e] In these research papers two fundamental questions perturbed us. The first one was how in aqueous/semi aqueous media the HSO_4^- acted as a hydrogen (H^+) acceptor in spite of its low pK_a value of 1.99[2h] and its competing nature with water.[6] The second question was why only blue shifts were observed in UV-visible spectra of most of the above Schiff-base receptors upon their binding with HSO_4^-.

Hence we went on to re-examine the mechanistic aspect of these Schiff-base receptors already reported in literature[3] for their HSO_4^- sensing. In this context first of all we were drawn to one of the recently reported fluorescent Schiff-base receptors reported by Kim *et al.*[3a] According to this report a Schiff base containing a coumarin (receptor **1**; λ_{max} = 355 nm), gave highly selective and sensitive turn-on fluorogenic response towards HSO_4^- in aqueous solution (λ_{max} = 370 nm, λ_{em} = 485 nm). Two analogues (receptors **2** and **3**; Fig. 1) were also prepared by the same workers and their fluorescent properties were also examined in the same fashion. Upon addition of HSO_4^- to **2** the observed fluorescence changes were marginal and non-selective. Receptor **3** (λ_{max} = 375 nm) showed weak fluorescence which increased in the presence of HSO_4^- (λ_{em} = $\sim$ 430 nm), as noted for receptor **1**.

According to Kim *et al.*, ^{1}H NMR studies and DFT calculations revealed that hydrogen bonding between the phenolic –OH and imine nitrogen of receptor **1** played a crucial role in its high selectivity towards HSO_4^-. The rupture of this intramolecular hydrogen bonding and formation of intermolecular hydrogen bonding in receptors **1** and **3** upon their interactions with HSO_4^- were proposed to be the plausible reason for its fluorescent detection. It should be noted, however, that the ^{1}H NMR studies were performed in CD_3CN while UV-visible and fluorescence investigations were performed

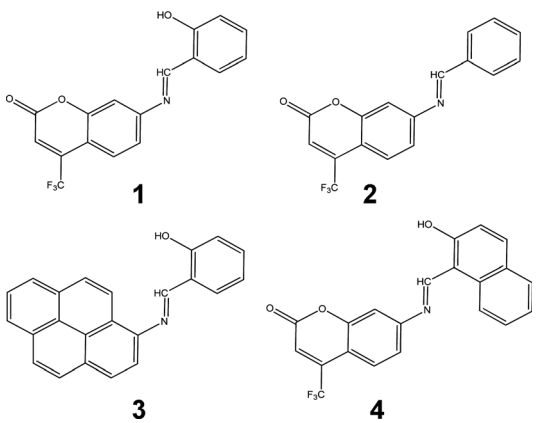

Fig. 1 Fluorescent receptors (**1–3**) for HSO_4^- synthesized by Kim *et al.* and by us (receptor **4**).

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in CH_3CN–H_2O (1 : 1, v/v) mixture. This variation of solvents in the above studies led Kim and co-workers to assign the sensing effect as being due to hydrogen bonding without exploring other plausible possibilities. In 2007, Kim and co-workers had suggested that the acidity of the HSO_4^- anion in water may be responsible for its different behaviour towards bis(indolyl)calix[4]crown-6 as compared to basic anions such as F^-, CH_3COO^- *etc*. Indeed, as stated above, the literature pK_a value of HSO_4^- is 1.99 (in aqueous medium)[2h,7] and it must behave as a hydrogen (H^+) donor in aqueous/semi-aqueous medium instead of accepting H^+ as for basic anions such as F^-, CH_3COO^- *etc*.

Hence, we resynthesized receptor **1** (Fig. 1) as described by Kim *et al*. and investigated its ^{1}H NMR spectral behavior in CD_3CN–D_2O (1 : 1, v/v) in the presence of HSO_4^-. Surprisingly, we observed hydrolysis of receptor **1**, as we observed the peaks for the corresponding aldehyde and amine (see Fig. S1†; due to presence of D_2O the signal for –OH of salicylaldehyde was not observed). We thus performed a further experiment in which we added HSO_4^- to receptor **1** solution in CH_3CN–H_2O (1 : 1, v/v) and left to hydrolyse for 3–4 h. After extraction with diethyl ether and evaporation we characterized the recovered product through ^{1}H NMR as the amine counterpart of the receptor **1** *i.e*., 7-amino-4-trifluoromethylcoumarin (Fig. S2†).

Hence the above studies showed evidence for hydrolysis of the Schiff base instead of any hydrogen bonding adduct as was reported by Kim *et al*. due to non-consideration of water in their ^{1}H NMR studies. The hydrolysis of the Schiff base in the presence of HSO_4^- was further supported by mass spectral studies for receptor **1** + HSO_4^-. This showed a molecular ion peak for the corresponding aldehyde and amine (Fig. S3†). The mass spectrum showed no peak for either receptor **1** or its HSO_4^- complex.

To further establish the above hydrolysis mechanism we synthesized a new Schiff-base receptor **4** (see Fig. 1) having the same amine *i.e*., 7-amino-4-trifluoromethylcoumarin (fluorescent constituent) but different aldehyde counterpart (2-hydroxynapthaldehyde instead of salicylaldehyde). Receptor **4** was characterized through various spectroscopic methods along with single-crystal X-ray diffraction study (Fig. S4–S8; Table S1†). Indeed, preliminary investigations of visual responses of **4** towards HSO_4^- were similar to that of **1**. We then performed more detailed UV-visible and fluorescence titrations of HSO_4^- and receptor **4** in CH_3CN–H_2O (1 : 1, v/v). Interestingly the UV-visible absorption and fluorescence emission bands were observed at almost the same wavelengths (λ_{max} = 369, λ_{em} = 487 nm; Table 1) as was found for receptor **1** by Kim *et al*. The λ_{max} for the complex **1** + HSO_4^- and **4** + HSO_4^- were at 370 and 369 nm while λ_{em} were observed at 485 and 487 nm respectively (Fig. S9 and S10†). This similarity of observations in terms of λ_{max} and λ_{em} even after changing the aldehyde constituent of receptor **4** also suggested the hydrolytic mechanism of sensing proposed by us rather than by hydrogen bonding as suggested previously. Since receptors **1** and **4** both possess the same amine counterpart *i.e*., 7-amino-4-trifluoromethylcoumarin, hence in both cases we observed λ_{max} and λ_{em} at almost the same wavelengths, around 370 and 485 nm, respectively. The same amine

Table 1 Observed and reported λ_{abs} and λ_{em} of starting materials and of receptors **1**, **3** and **4** with various analytes[a]

Entry	λ_{abs}/nm	λ_{em}/nm
7-AMC	370[b]	486[b]
1	355[3a]/358[b]	Almost NF
1 + HSO_4^-	370[3a]/371[b]	485[3a]
4	450, 476[b]	Almost NF
4 + HSO_4^-	369[b]	487[b]
1-AMP	340[b]	430[b]
3	375[3a]/380[8]	Almost NF
3 + HSO_4^-/Hg^{2+}	340[3a,8]	~430[3a,8]

[a] UV-visible data were measured at 50 μM while fluorescence data were obtained at 3 μM in CH_3CN–H_2O (1 : 1, v/v) solution; NF = non-fluorescent; 7-AMC = 7-amino-4-trifluoromethylcoumarin; 1-AMP = 1-aminopyrene. [b] This work.

absorbs at λ_{max} = 370 nm while it emits at λ_{em} = 485 nm in CH_3CN–H_2O (1 : 1, v/v) (Fig. S9 and S10†).

When we carried out ^{1}H NMR studies upon addition of HSO_4^- to receptor **4** in CD_3CN–D_2O we observed peaks for the individual amine and aldehyde similarly to above for **1** + HSO_4^- (Fig. S11†). Moreover the ^{1}H NMR (Fig. S12†) and ESI mass spectrum of extracted products as above in the case of receptor **1**, clearly supports the hydrolysis of receptor **4** into its constituents (Fig. S13†). The changes in absorption and emission wavelengths of receptors (**1**, **3** and **4**) before and after binding with HSO_4^-/Hg^{2+} are summarized in Table 1.

We tried to co-relate the above observations with one yet another piece of work by Kim *et al*. published in 2010.[8] In this work they proposed a chemodosimetric approach (hydrolysis of Schiff base) for the sensing of Hg^{2+} through the same Schiff-base receptor **3** as mentioned above in CH_3CN–H_2O (9 : 1, v/v). The corresponding fluorescence changes in the receptor **3** by Hg^{2+} matched excellently well with the case of **3** + HSO_4^- (λ_{max} = 341 nm λ_{em} = 430 nm; see Fig. S14†). The amine counterpart of the receptor **3** *i.e*., 1-aminopyrene absorbs at 340 nm[8] and fluoresces at 430 nm (see Fig. S15†) which matched well with that of **3** + HSO_4^- and **3** + Hg^{2+}.[3a,8] Two different mechanistic pathways by Kim *et al*. for fluorogenic sensing of Hg^{2+} and HSO_4^- by the same receptor **3** are very difficult to understand. Hence our proposal of hydrolytic mechanism for the sensing of HSO_4^- by Schiff-base receptors in aqueous medium was further strengthened. In the light of above discussions the fate of receptor **1** and **3** in the presence of HSO_4^- and other analytes can be summarized conveniently through Schemes 1 and 2 in ESI†.

Kim *et al*. extended their similar research work later on with a few other Schiff-base receptors for the detection of a variety of metal ions *viz*., Cu^{2+} and Fe^{3+} *etc*.[9] The lability of >C=N towards hydrolysis under the influence of above metal ions was made the basis for sensing. In analogy to Kim's work with metal ions, HSO_4^- can also have a similar hydrolytic effect due to its ability to release H^+, a factor which is often overlooked. In fact the smaller charge/size of H^+ than Cu^{2+}, Fe^{3+} and Hg^{2+}, provides it good acidic character. Since the hydrolytic cleavage of Schiff bases were observed by a number of metal ions we also performed similar studies on receptors **1** and **4**. Out of the various metal ions only Al^{3+} was found to be effective (Fig. S16†). The hydrolysis of receptor **3** was also observed in the presence of Al^{3+}, which was not considered by

Table 2 Reported λ_{abs} of starting materials and of receptors **5** and **6a–d** with various analytes

Entry	λ_{abs}/nm
5-PASA	341[12]
Receptor **6a**/**6b**	**6a** = ~350 (s), ~480 (w)[3c]
	6b = ~330 (s), ~480 (w)
6a/**6b** + HSO_4^-	~340
5-PNSA	376[3b]
5	376, 480[3b]
5 + HSO_4^-	370
Receptor **6c**/**6d**	**6c** = ~380 (m), ~540 (s)[3c]
	6d = 412 (w), 530 (s)
6c/**6d** + HSO_4^-	~374

5-PASA = 5-(phenylazo)salicylaldehyde; 5-PNSA = 5-(*p*-nitrophenylazo)salicylaldehyde, w = weak, m = medium, s = strong.

Kim *et al.* in their studies. Here it should be noted that not all the Schiff bases undergo this type of hydrolysis with every metal ion. Our own report showed Al^{3+} enhanced fluorescence of a Schiff-base receptor.[5a] The work of Lehn's *et al.*[10] and others[11] have presented an excellent account in this context.

On the similar line to the above fluorescent Schiff-base receptors we went through a number of reports[3b–e] involving colorimetric Schiff-base receptors for HSO_4^- detection. Such receptors are different from the fluorescent ones in terms of not having any fluorescent constituents *i.e.*, aldehyde or amine, rather they behaved as strong intramolecular charge transfer (ICT) probes and absorbed towards higher wavelengths. All these receptors were reported to undergo bleaching with HSO_4^- and thus exhibited blue shifting in their UV-visible spectra. However bathochromic shifting has been reported for genuine hydrogen bonded cases of anions with receptors. This differing observation led us to think once again in terms of a hydrolytic mechanism as we have discussed above. The mechanistic details of interactions of colorimetric Schiff-base receptors (receptors **5** and **6**; reported by Wei *et al.* and Zhang *et al.*, Fig. S17†) with HSO_4^- are discussed in detail (see ESI†; Discussion section). The corresponding absorption changes of these receptors before and after binding with HSO_4^- are given in Table 2.

Hence, our above discussion and experimental evidences clearly proved that the hydrolysis of Schiff-base receptors through HSO_4^- in aqueous media was the key step towards the sensing rather than hydrogen bonding as claimed previously. The overall effect of HSO_4^- on Schiff-base type receptors is highly dependent on the solvent in which the experimental studies are carried out as it plays the key role in deciding the acidic/basic character of an amphiphilic ion such as HSO_4^-. So the role of solvents cannot be ignored in the above type of sensing phenomenon. It is clearly necessary to maintain the same solvent medium throughout entire experimental studies while establishing a mechanism for its action.

In conclusion, we were successful in establishing that hydrogen bonding between HSO_4^- and Schiff-base receptor was not the determining factor in the sensing mechanism in aqueous medium as reported previously. Rather, hydrolysis of the Schiff-base receptor by a sufficiently strong acid such as HSO_4^- in aqueous medium is responsible. The present study further establishes that the Schiff-base type receptors may prove to be good candidates for selective and sensitive detection of HSO_4^- in aqueous medium.

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