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The fluorescence Quenching Study of Quinine in Presence of Some Anions

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Abstract: The quenching of quinine fluorescence intensity in the presence of some anions in aqueous solution at ambient temperature has been investigated. The quenching is found to be collisional or dynamical in nature. This study reveals the order of two groups of quencher: NaI > NaBr > NaCl > NaF and $K_2Cr_2O_7$ > $KMnO_4$ >Na_2SO_4 > $NaClO_3$. Increasing anion size in the both groups leads to an increase in the quenching due to deactivation processes. As heavy and multi-core anions have greater influence on the quinine's fluorescence than light halide anions and NaF hasn't any effect on the fluorescence intensity. The quenching follows linear Stern–Volmer relation. The values of Stern–Volmer quenching constants/quenching efficiencies (K_{sv}) for the anions were found to be 2385, 436, 354, 0, 1398, 853, 238, 218 M^{-1} respectively. Statistical analysis by linear regression method confirms significant different among the values of Stern–Volmer quenching constants.

Key words: Quinine, Quenching, fluorescence, Stern-Volmer constant

1. Introduction

Fluorescence quenching has been widely studied as a fundamental phenomenon and in the application of fluorescence to biochemical problems. Quenching measurement can reveal the accessibility of fluorophores to quencher. Fluorescence quenching refers to any process which decreases the fluorescence intensity of a certain fluorophore. A variety of processes can result in such decreasing in intensity involving collisional or dynamical quenching, static quenching and etc. Dynamic quencher occurs in association with collision between fluorophore in its excited state and quencher molecule.

The fluorophore returns to ground state without emission of light. On the other, in static quenching a non-fluorescent complex is formed between the fluorophore and the quencher. Usually only a fluorophore which is not complexed can exhibit fluorescence.

Hence, in case of complex formation there is a frequently change in absorption spectrum of the fluorophore, whereas dynamic quenching occurs in fluorophore excited state and so only the life time of the excited state is reduced. Dynamic fluorescence quenching is a diffusion process and therefore, is also influenced by the solvent viscosity and temperature that influence on the excited state. If the used solvent is very viscous, diffusion is slow, so the quenching is inhibited in a controlled diffusion process. On this basis, the study of quenching can reveal the diffusion rate of quenchers. If a fluorophore bound either to a protein or a membrane, which is impermeable to the quencher, or if the fluorophore is located in the interior of the macromolecule, quenching of fluorescence parameters cannot occur. On the other hand, the fluorophore bound to a permeable membrane to quencher would show change in fluorescence parameters in the presence of quencher. For this reason quenching studies can be used to reveal the localization of fluorophores in protein and membranes and their permeability to quencher [1]. As in both cases, the fluorescence intensity is related to the concentration of the quencher. Therefore, the quenched fluorophore can serve as an indicator for quenching agent.

The dynamic or static fluorescence quenching can be described by the Stern–Volmer equation as follows:

$$I_0 / I = \tau_0/\tau = 1 + K_{sv}[Q] \qquad (1)$$

Where, I and I_0 are the fluorescence intensities in the presence and absence of a quencher, respectively. The quenching constant or Stern–Volmer constant (K_{sv}) for static quenching is identical with association constant of the formed complex between fluorophore and quencher, [Q] is concentration of the quencher, τ and τ_0 are the lifetimes of the excited state of the fluorophore in the presence and absence of the quencher, respectively.

The occurrence of quenching depends upon the mechanism, which in turn depends upon the structure of the individual molecules. Detailed analysis of the mechanism of quenching is complex. Fluorescence materials are currently used for a wide variety of sensing applications [2-12].

The quenching of fluorescence intensity is one of the most common techniques [2, 3, 13–18] for the sensing of humidity and gases. It is of great interest to develop optical sensors for various ions like metal and halide ions. Naryanaswamy et al. [2] were reported a fluorescence intensity-based system (quinine sulphate, acridine and SPQ ([6-methoxy-N-(3-sulfopropyl) quinolinium]).

In another work, Geddes and Geddes et al. [3–6] were reported quenching of some dye, e.g. rhodamine6G, SPQ and 6-methoxyquinoline in the presence of halide ions.

In this paper we study the quenching behavior of quinine-H_2O_2 system in aqueous media in the presence of some ions by using of fluorescence parameters (fluorescence intensity and quenching constant). Quinine is a natural white crystalline alkaloid. The structure of quinine is shown in Fig. 1.

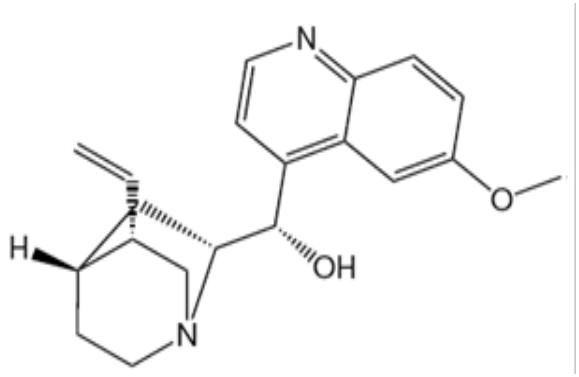

Fig. 1. Chemical structure of quinine [19].

The compound is stable in solution and emits blue light when it is excited in the near UV. It has antipyretic, antimalarial, analgesic properties and a bitter taste and has been use for over three centuries [19]. It is a highly fluorescent and organic molecule that has been widely used as a fluorescence quantum-yield standard [20].

It adds to tonic water in safe and trace quantities as flavors. Despite these benefits, quinine blocks compound Ca^{2+}-activated K^+ channels [21] and Ca^{2+}-activated K^+-dependent swelling of mitochondria [22]. The high level of quinine in drinks can lead to blindness. Hence, the study of quinine's fluorescence properties in the presence of different ions can play a significant role at the interpretation of quinine's fluorescence in different matrixes and access to accurate result.

2. Experimental

Quinine hydrochloride was purchased from Fluka. The quinine concentration in 0.05M H2SO4 for measurements was 10^{-3}M. Sodium fluoride, sodium chloride, sodium bromate, sodium iodate, sodium sulfate, potassium permanganate, sodium perchlorate and potassium dichromate (all materials from Merck) were dissolved in water to prepare various concentrations of anions.

The absorption and fluorescence spectra were recorded using UV–Vis CECIL 5505 spectrophotometer and Perkin Elmer LS3 spectrofluorometer, respectively.

3. Results and discussion

Stern and Volmer described this type of quenching as a bimolecular process that competes with radiative decay, and offered an equation to express the phenomenon [23].

The equation was based on the following kinetic scheme:

$$D + h\nu \rightarrow D^* \quad (2)$$

$$D^* \xrightarrow{k_1} D + h\nu \text{ or } \Delta \quad (3)$$

$$D^* + Q \xrightarrow{k_2} D + Q + \Delta \quad (4)$$

$$D + Q^* \rightarrow D + Q + \Delta \quad (5)$$

$$D^{++} + Q^{-} \rightarrow D + Q + \Delta \quad (6)$$

$$D^{-} + Q^{+} \rightarrow D + Q + \Delta \quad (7)$$

Where D is the ground-state species, D* is the excited-state species, and Q is the quencher. k_1 is the first-order rate constant for decay of the excited state (eq 3), and k_2 is the sum of the bimolecular rate constants for all processes depleting the excited state including catalytic deactivation (eq 4), energy transfer (eq 5), and electron transfer (eqs 6, 7).

The fluorescence and absorption spectra of quinine are shown in Fig. 2.

The observed fluorescence emission maximum is 437nm. Addition of halide ions and other ions such as MnO_4^-, SO_4^{2-} and ClO_3^- can decrease the intensity of emission spectra without any effect on the position of emission maxima. Also, the shape and full-width at half maximum (FWHM) of the absorption and emission bands remain unchanged. Hence, it may be considered that the process of quenching is dynamic in nature and a diffusion controlled bimolecular process is responsible for the observed quenching. This ruled out the possibility of a chemical reaction between anions and quinine.

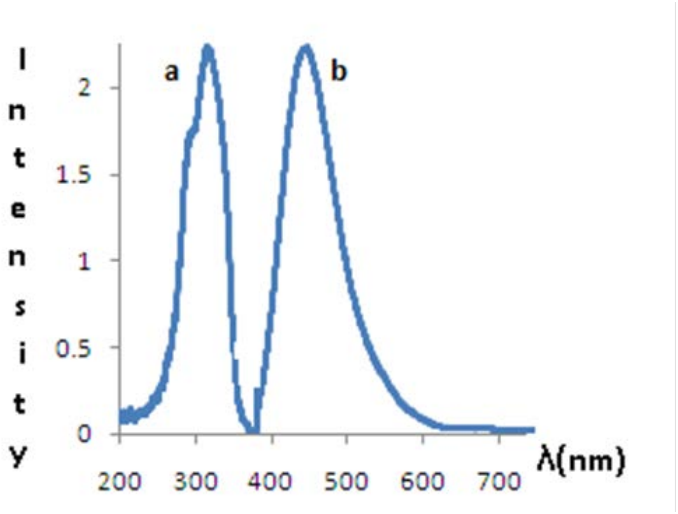

Fig. 2. Absorption (a) and emission (b) spectra of quinine.

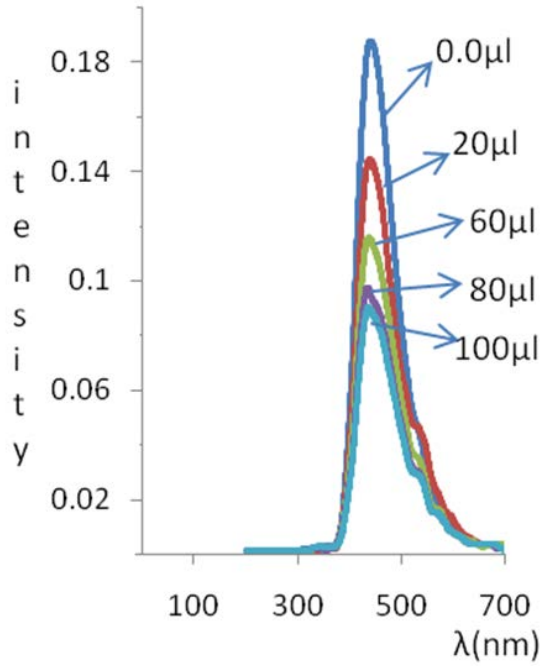

Fig. 3. The changing fluorescence emission spectra of quinine (10^{-3}M) in aqueous solution with addition of 0.0, 20, 60, 80, 100 µl Cl^- (10^{-1}M).

It is notable mention that the change in pH value of the quinine solution during measurements was considerably small for all of anions concentration. The decreasing of quinine fluorescence intensity in aqueous solution with increasing concentration of Cl^- and MnO_4^- ions are shown in Fig.3 and Fig.4, respectively.

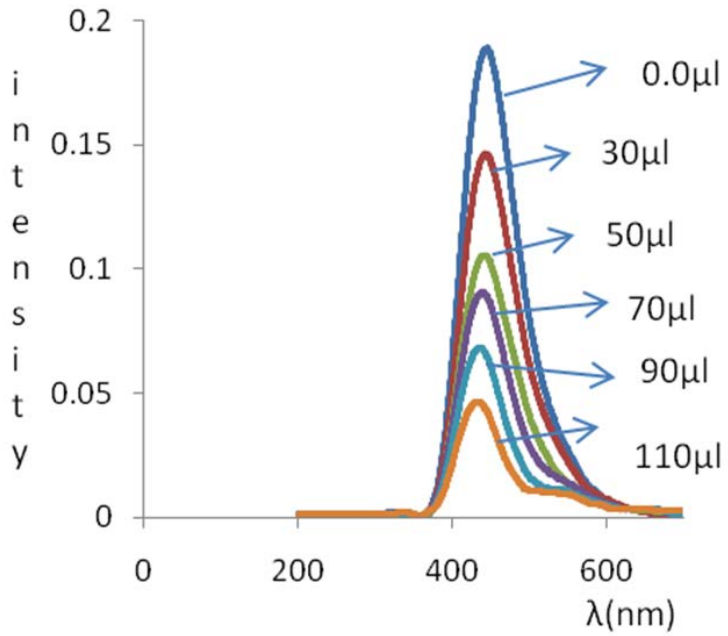

Fig.4. The changing fluorescence emission spectra of quinine (10^{-3}M) in aqueous solution with addition of 0.0, 30, 50, 70, 90, 110 µl MnO_4^- (10^{-1}M).

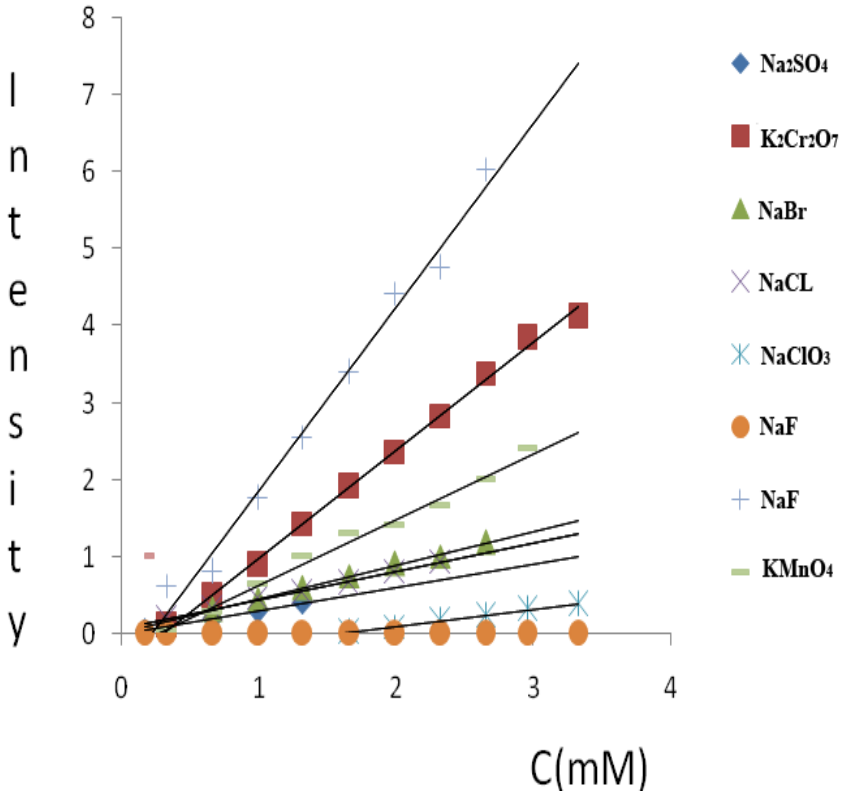

Fig. 5. Stern–Volmer plot.

The addition of anions (0.1 mM) to quinine solution causes a considerable change in the fluorescence intensity.

It can be resulted from Fig.3 that the emission intensity is decreased successively with increasing chloride ion concentration.

We can follow decreasing of fluorescence intensity with stern-volmer equation (1). If a plot of I_0/I - 1 vs [Q] is constructed, the data should be linear with a slope equal to K_{sv}. Considering the slope, we can compare influence of quenchers. Fig.5 shows I_0/I - 1 vs. [Q] for the used different anions and table 1 summarizes linear equations of different anions and the values of K_{sv} for them. As it is obvious of Table 1, there is an increase at the value of quenching constant with increasing molecular of weight or size of anions in both groups of anions (halide and multi-core anions). Also, multi-core anions have greater influence on the quinine's fluorescence than light halide anions.

It seems the quenching is due to deactivation process. Increasing of anion size or molecular of weight induces intersystem crossing that it causes a dynamic quenching. So, the process of halide ions and other ions quenching confirms it.

In order to compare the values of Ksv, statistical analysis based on linear regression method was performed [24]. The result (table 1) proves significant different among the values of Ksv or the anions effect on quinine fluorescence intensity.

Table1. Linear equation and regression parameters (at %95 confidence interval) of different anions.

Anion	Linear equation	$\mathbf{k_{sv}}$	**CV**	$\mathbf{R^2}$
NaI	Y=2385X-0.510	2385 ± 4.42	0.095	0.986
$K_2Cr_2O_7$	Y=1398X-0.412	1398 ± 2.19	0.083	0.997
$KMnO_4$	Y=853.5X-0.222	853.5 ± 3.23	0.199	0.990
NaBr	Y=436.9X-0.024	436.9 ± 2.06	0.23	0.997
NaCl	Y=372X+0.07	372 ± 4.04	0.53	0.992
Na_2SO_4	Y=301X+0.007	301 ± 3.195	0.49	0.994
$NaClO_3$	Y=218.5X-0.338	218.5 ± 2.13	0.45	0.998
NaF	Y=0.0	0.0	_	_

4. Conclusion

This study determined the process of halide ions and other anions effect as quenchers on the quinine fluorescence intensity based on Stern–Volmer constants:

NaI › NaBr › NaCL › NaF

$K_2Cr_2O_7$ › $KMnO_4$ › Na_2SO_4 › $NaClO_3$

It was found that K_{sv} increases with increasing of anion size. Consequently, the quenching increases with the increasing size of the anions. As the greatest decrease in fluorescence intensity is obtained in the presence of NaI, and NaF has not any effect on the fluorescence intensity of quinine. The received results are compatible with the rules due to dynamic quenching.

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