MEASUREMENT OF HYDROGEN CHLORIDE GAS USING FLUORESCENCE QUENCHING

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ABSTRACT

Fluorescence quenching of benzopurpurin (BP) by HCl in methanol is investigated. The observed extremely efficient quenching is attributed to the formation of a non-fluorescent exciplex between BP and HCl. Other pollutant gases, such as H_2S and NH_3, were found not to effect the fluorescence of BP. Possibilities of using this finding to develop a fibre optic HCl sensor are discussed.

1. INTRODUCTION

Hydrogen chloride (HCl) is one of the primary local air pollutants made by man. Concentrations of 5 ppm in air have been recommended as threshold limit value (TLV) for human exposure. The exposure for a few minutes to HCl concentrations of 1200-1300 ppm can be lethal to humans. A number of anthropogenic sources of HCl include pesticide manufacturing, HCl production plant and chlorinated polymers. It is known that pyrolysis of polyvinylchloride (PVC) results in complete removal of chlorine from the polymer backbone in the form of HCl. Reports are available which suggest that one kilogram of PVC polymer yields 580 g of HCl[1]. Given the high usages of chlorinated polymers, a fast, reliable, easy to perform and cost effective method for the measurement of HCl concentration is needed. It is also desirable that such a method can be used for on-line and for the remote monitoring of HCl.

Both off-line and on-line methods for quantitatively measuring HCl concentrations are known. The conventional discontinuous methods depend on the spectroscopic measurement of the dye complexes formed by reagents and hydrogen chloride or iodometric titration. A method of HCl measurement based on the use of a chloride ion selective electrode is reported by Staden[2]. Another method of monitoring HCl uses a zinc coated pizo-electric quartz crystal. Exposure to HCl leads to the formation of $ZnCl_2$, and the resulting frequency change of the piezoelectric quartz crystal is related to HCl concentration[3] . However, such methods are tedious, time consuming and require expensive instrumentation.

In continuation to our work on molecular fluorescence and its diagnostic applications[4-6], we report in this paper on an extremely efficient quenching of benzopurpurin by HCl. Possibilities of constructing a fibre optic HCl sensor are discussed.

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2. EXPERIMENTAL

2.1. Materials.

Benzopurpurin and other chemicals employed in this investigation were from Aldrich Chemical Co. and were used without further purification (after checking their absorption spectra). Methanol was doubly distilled and dried over $CaCl_2$. Concentrated hydrochloric acid was used. (dry HCl gas dissolved in methanol and hydrochloric acid in methanol gave similar results)

2.2. Instrumentation.

Absorption spectra were recorded, using a Perkin-Elmer λ5 spectrophotometer in a 1 cm path length quartz cuvette. The fluorescence spectra were recorded on a Perkin-Elmer LS-5 spectrophotofluorimeter which was equipped with a Hamamatsu photomultiplier R928P as detector.

Fluorescence quenching measurements were made by recording a series of standard solutions in which the concentration of HCl ranged from 0 to 2000 μM. The concentration of benzopurpurin was kept constant at 15 μM to avoid self-quenching or inner-filter effects. The excitation wavelength was 465 nm for these spectra. A 2 nm bandpass was used throughout, for both the excitation and emission monochromators. All measurements were made in a standard quartz sample cell (1 x 1 cm) at room temperature (22 ± 1 °C).

2.3. Preparation of HCl Solutions

HCl stock solution in methanol was prepared by adding conc. hydrochloric acid in methanol. Final concentration of the stock solution was 0.1 M, which was determined by iodometric titration. Desired dilutions were made from this stock solution to perform further experiments.

3. RESULTS AND DISCUSSIONS

Excitation and fluorescence spectra of benzopurpurin in methanol are given in fig. 1. It has a broad excitation (ca. 300-600 nm) with a peak at 465 nm and emission (ca. 640-780 nm) with a peak at 681 nm.

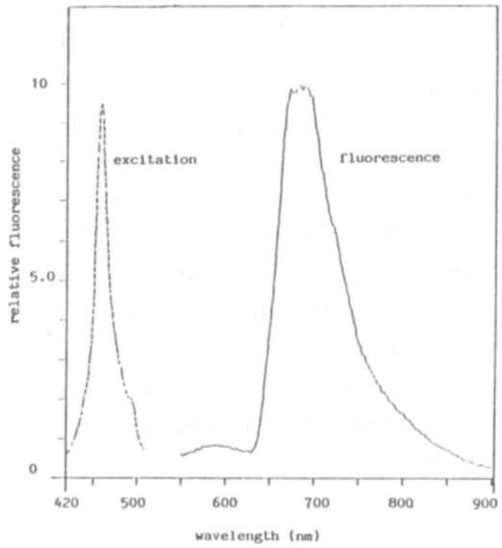

Figure 1 Excitation and fluorescence spectra of benzopurpurin in methanol

The ability of HCl to quench the fluorescence of benzopurpurin was studied in a series of experiments. The methanol solutions, having constant indicator concentration of 15 uM and varying quencher concentrations, were excited by a radiation of wavelength 4655 nm. These experiments revealed that the fluorescence intensity of benzopurpurin decreases as the concentration of HCl increases. The fluorescence quenching data have been analyzed according to the Stern-Volmer relationship:

$$I_o / I = 1 + K_{sv} [Q]$$

where I_o and I are the fluorescence intensities in the absence and presence of the quencher, K_{sv} is the Stern-Volmer quenching constant and [Q] is the concentration of the quencher. Figure 2 shows the Stern-Volmer plot for HCl quenching data collected with an emission wavelength setting of 681 nm. A downward curvature at quencher concentrations above 0.2 mM is seen in this plot. A K_{sv} value of $3 \times 10^3\ M^{-1}$ is obtained by linear regression analysis of the initial part of the curve.

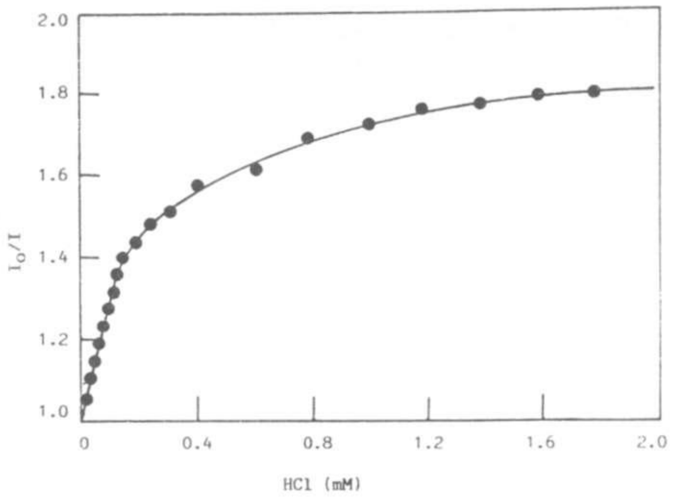

Figure 2. Stern-Volmer plot of the quenching of benzopurpurin by HCl in methanol

The above information reveals that HCl is an extremely efficient quencher of benzopurpurin. But at higher quencher concentrations fluorophore is not accessible to the quencher. This is unlikely in fluid solutions and is possible only when a fluorescence complex is formed which is not quenched by HCl. Another possibility which may result in negative curvatures is the formation of a reversible exciplex. Our initial findings suggest that such possibilities exist in the case of the present fluorophore-quencher combination[7].

The finding that HCl is an extremely efficient quencher of the fluorescence of benzopurpurin can be exploited to measure low HCl concentrations in industrial and environmental applications. The possibility of making HCl measurements in air and missile launch sites, is of particular interest. The measurement of BP fluorescence, and consequently the quenching of this fluorescence by HCl, is possible. This is especially attractive, since other major pollutant gases, such as H_2S, and NH_3 do not interfere in the measurement. SO_2 interference can be avoided, by using a HCl selective membrane or by employing another indicator, which is not quenched by HCl, and mathematically separating the signals. A simple device to monitor HCl dissolved in liquids/gases based on HCl quenching of benzopurpurin is possible. Optical properties of benzopurpurin are well suited for the use of simple, inexpensive and durable solid state optoelectronic components. In addition, the broad features of the excitation and emission spectra provide a great deal of flexibility in designing the optics for a particular application. These features suggest that a compact and inexpensive instrumentation can be readily developed for HCl measurements based on benzopurpurin fluorescence quenching. Corresponding work is in progress.

4. ACKNOWLEDGMENTS

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5. REFERENCES

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Note: Benzopurpurin 4B has shown concentration dependent spectral shifts and this behaviour is being investigated.