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APPLICATIONS OF FLUORESCENCE QUENCHING TO QUANTITATIVE ANALYSIS: ANALYSIS OF METHANOL- ISOPROPANOL AND METHANOL- DEUTEROMETHANOL MIXTURES BY THE QUENCHING OF URANYL ION LUMINESCENCE

The possibility of using the quenching of uranyl ion luminescence in the analysis of binary alcohol mixtures is investigated, and it is shown that this can provide a cheap, rapid method for such analyses. The method is suitable for analysis of mixtures of deuterated and non-deuterated alcohols, and can be adapted to the analysis of other species which quench uranyl ion luminescence.

1 — INTRODUCTION

Numerous examples have been presented in the literature of the quenching of luminescence in solution by such processes as energy transfer, electron transfer, and atom transfer. In the majority of cases the quenching follows Stern-Volmer kinetics [1], such that the ratio of the fluorescence intensities in the absence (I^0) and presence (I) of a quencher molecule is a function of its concentration (c):

$$I^0/I = 1 + K_{sv}c \quad (1)$$

K_{sv} is a constant for a given quencher. Since the extent of quenching is a function of the quencher concentration, the technique provides a potentially useful method for quantitative analysis. Perhaps surprisingly, only a few examples of such a use have been reported [2-6]. One application is the use of the quenching of the fluorescence of pyrene by molecular oxygen in the determination of dissolved oxygen concentrations [2]. In addition, selective quenching has been shown to be potentially useful in the fluorescence analysis of mixtures of fluorescent compounds [5,6]. The technique has the advantages that it can be a fairly cheap, rapid method for small (μ l) quantities of compounds, and can readily be used in the analysis of volatile compounds which are difficult to study by other methods (e.g. possessing no characteristic ultraviolet absorptions). The method may, in principle, readily be automated to make it suitable for batch analysis. Against these advantages, the technique, like other kinetic methods of analysis [7], is not very selective.

There has recently been considerable interest in the photochemistry of the uranyl ion [8-10]. One of the important types of photoreaction of this species involves bimolecular interaction between photoexcited uranyl ion and substrate, followed by oxidation of the substrate by either electron or atom transfer. This interaction is accompanied by the quenching of the well characterized uranyl luminescence [11], the kinetics of which follow good Stern-Volmer kinetics. The quenching efficiency, as measured by the slope of the Stern-Volmer plot, is very sensitive to the nature of the substrate, and a wide variety of quenching constants have been observed. Further, the uranyl luminescence is unaffected by the presence of oxygen, suggesting that the quenching

of its luminescence may be a convenient method for quantitative analysis in certain cases. A report has already been presented [4] on the use of the quenching of UO_2^{2+} luminescence in the microanalysis of iodide ion.

In the quenching of uranyl luminescence by alcohols [11], the quenching is thought to proceed via hydrogen atom abstraction from the alcohol [10], and the rate of this is found to depend markedly on the C-H bond energy of the alcohol. There is also a significant deuterium isotope effect [11,12]. The rate of hydrogen abstraction can vary by up to three orders of magnitude, depending on the nature of the substrate.

In the present study, we have made these observations a basis for a method of quantitative analysis of binary alcohol-alcohol systems. Since water is frequently the solvent of choice, the analyses can readily be extended to alcohol-water systems, or to other binary systems involving species which quench uranyl ion luminescence.

2 — EXPERIMENTAL

2.1 — REAGENTS

Uranyl nitrate hexahydrate (reagent grade, greater than 98% purity), «Proanalysis» grade alcohols, and deuteromethanol (for n.m.r.) were used without any further purification. Various concentrations (percentage by volume) of binary isopropanol-methanol mixtures were prepared by pipetting a known volume of one component into a volumetric flask and adding the other component to give the standard volume. No significant volume contraction effect was observed with this mixture. Such an effect is, however, likely to be of importance in alcohol-water systems, and in such cases we recommend that known volumes of the same component are always pipetted into the flask. With methanol-deuteromethanol mixtures, microlitre quantities of the two components were added in a fixed ratio by using two microsyringes.

2.2 — APPARATUS

Luminescence spectra were recorded of uranyl solutions in 10 mm quartz cells using a Perkin-Elmer MPF-3 spectrofluorimeter. An excitation wavelength of 436 nm was used for all studies.

2.3 — GENERAL PROCEDURE

Volumes varying between 1 and 25 μl of the alcohol mixtures were added to a known volume (commonly 3.0 ml) of a solution of uranyl nitrate (2×10^{-3} M) in water in a fluorimeter cell, and the luminescence spectrum of the solution obtained. The addition of such small quantities of quencher has no significant effect on the overall volume of the solution. To minimise photooxidation of substrate by UO_2^{2+} , solutions were only exposed to the excitation lamp when the spectra were actually being recorded. The uranyl emission consists of a series of bands around 500 nm, and in these studies the intensity of the band at $515(\pm 5)$ nm was studied as a function of quencher concentration. A normal Stern-Volmer treatment [1] was used to analyse the quenching data, and good linear plots were observed in all cases. Slopes of the graphs of I^0/I against quencher concentration (measured as percentage by volume of total solution in the cell) were determined by conventional least squares treatment. Normally 8-10 different quencher concentrations were used for each Stern-Volmer plot. Calibration curves were prepared of Stern-Volmer quenching constant against percentage alcohol concentration for different ratios of binary mixtures.

2.4 — EFFECT OF URANYL CONCENTRATION, TEMPERATURE AND pH

The Stern-Volmer quenching constant (K_{sv}) is a composite term consisting of both a quenching rate constant (k_Q) and the lifetime (τ) of the excited state being quenched,

$$K_{sv} = k_Q \tau \quad (2)$$

and both these terms are expected to be affected by changes in the physical conditions. The lifetime of uranyl luminescence has been shown to be a function of the uranyl concentration and of the temperature [13]. We have studied the quenching of uranyl luminescence by isopropanol as a function of uranyl concentration over the range 0.001 to 0.02 M, and have found that the quenching constant does not change significantly in this range. However, using values calculated from the data of KEMP *et al* [13] for the lifetime of uranyl luminescence in per-

chloric acid solution (Table 1), it can be seen that such effects are likely to be important at uranyl concentrations greater than 0.05 M. Because of the variation of uranyl lifetime with temperature, it is important that the cell is kept at a reasonably constant temperature. In the present study although the cell was not thermostated, the solution temperature

Table 1

Effect of uranyl ion concentration on the lifetime of the luminescence of uranyl nitrate in aqueous perchloric acid (0.233 mol dm⁻³)

[UO ₂ ²⁺]/mol dm ⁻³	Lifetime/ μ s ^{a)}
0.001	6.56
0.01	6.41
0.05	5.81
0.1	5.21
0.5	2.84
1.0	1.81

^{a)} Calculated from data in ref. [13].

was found to vary by, at the maximum, 2-3°C, and such variations did not significantly affect the quenching. The quenching of uranyl luminescence by ethanol is not significantly affected by pH in the range 1.5-3.5 [11] and no special attempt was made to buffer the solutions. The natural pH of the solutions was commonly 3.5-4.0.

2.5 — EFFECT OF WATER PURITY

Impurities in the solvent water which react with uranyl ion excited state are likely to decrease its lifetime, and, hence, K_{sv} . We have accordingly looked at the effect of the purity of the water on the quenching of the luminescence by isopropanol. The quenching constants for deionized (1.29) and singly distilled water (4.08) show that the purity of the water is very important. With triply distilled water, the quenching constant is even bigger. Since the sensitivity of the method will be affected by the magnitude of K_{sv} , the water should be of as high a grade of purity as possible. However, more important than the actual purity is the fact that the same grade of water is used for preparing calibration curves and for analysis. The low value of K_{sv} for deionized water must be associated with the presence of organic impurities leached from the column. A determina-

tion of K_{sv} for the quenching of UO₂²⁺ luminescence by isopropanol would, in fact, seem to be a rapid, cheap method for the testing of organic impurities in water.

3 — RESULTS AND DISCUSSION

The quenching of uranyl luminescence by a variety of methanol-isopropanol mixtures was studied, and the Stern-Volmer constants determined as a function of percentage (v/v) of one component in the mixture. The quenching constant was found to vary continuously as a function of concentration, and, in this way, a calibration curve could be obtained from which the concentration of any unknown methanol-isopropanol mixture could be determined. The slope varied by a factor of *ca* 5.5 between pure methanol and isopropanol. On the basis of the standard deviations of the Stern-Volmer plots, it was found that concentrations of unknown mixtures could be estimated to within 6-7%. It is probable that, by closer control of temperature, etc., a rather higher precision can be obtained. Simple kinetic analysis of the quenching of uranyl excited state by two species, Q₁ and Q₂, can relate the total Stern-Volmer quenching constant, K_{sv} , to the quenching constants and relative concentrations of Q₁ and Q₂. It is most convenient for the present systems to give their relative concentrations in percentage by volume. When dealing with a kinetic system, strictly it is necessary to talk about molar concentrations. Volume percentage will be proportional to the molar ratio only at constant temperature for ideal liquids. For mixtures of similar compounds, such as alcohols, the deviation from ideal behaviour is expected to be small. For components Q₁ and Q₂, with Q₁ at a concentration *x*% (v/v), the total Stern-Volmer constant is given by

$$K_{sv} = \frac{x}{100} \cdot K_{sv}^{(1)} + K_{sv}^{(2)} \cdot \frac{(100-x)}{100} \quad (3)$$

where $K_{sv}^{(1)}$ and $K_{sv}^{(2)}$ are the quenching constants for quenching by pure Q₁ and pure Q₂ respectively, expressed in the units of (percentage)⁻¹. Differentiation of equation (3) with respect to *x* gives

$$\frac{dK_{sv}}{dx} = \frac{K_{sv}^{(1)} - K_{sv}^{(2)}}{100} \quad (4)$$

clearly showing that the precision of the method depends on the differences in the Stern-Volmer constants. The method is thus likely to be most sensitive when this difference is as big as possible.

Results for a typical study of the quenching of uranyl luminescence by methanol-isopropanol mixtures are illustrated in fig. 1. Equation (3) predicts a linear relationship between K_{sv} and the percentage of isopropanol. However, the slight curvature seen in fig. 1 suggests that the kinetic treatment is rather an oversimplification. The most reasonable explanation is that the methanol-isopropanol system does not follow ideal behaviour, and that on mixing, the volumes of the alcohols are not strictly additive. For analysis using this method, experimental calibration curves should be employed.

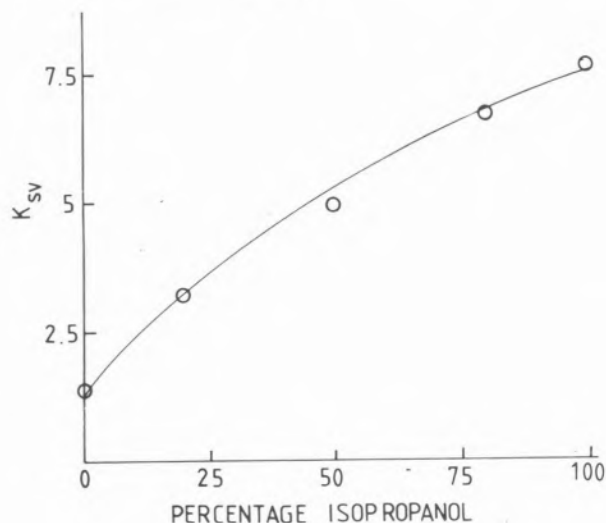


Fig. 1

Stern-Volmer constants for the quenching of the luminescence of uranyl nitrate ($2 \times 10^{-3} M$) in water (pH 4) by methanol-isopropanol mixtures as a function of the percentage of isopropanol (v/v)

The quenching of uranyl ion excited state by alcohols shows a pronounced deuterium isotope effect [12]. This suggested to us that it might be possible to analyse mixtures of protio- and deuterio- alcohols quantitatively by this method. We have, therefore, studied the quenching of uranyl luminescence by various mixtures of methanol and deuteromethanol (fig. 2). An isotope effect of 2.85 was observed in the present study, in good agreement with previous reports [12] on this system. From the curve, it is clear that the method can readily be used

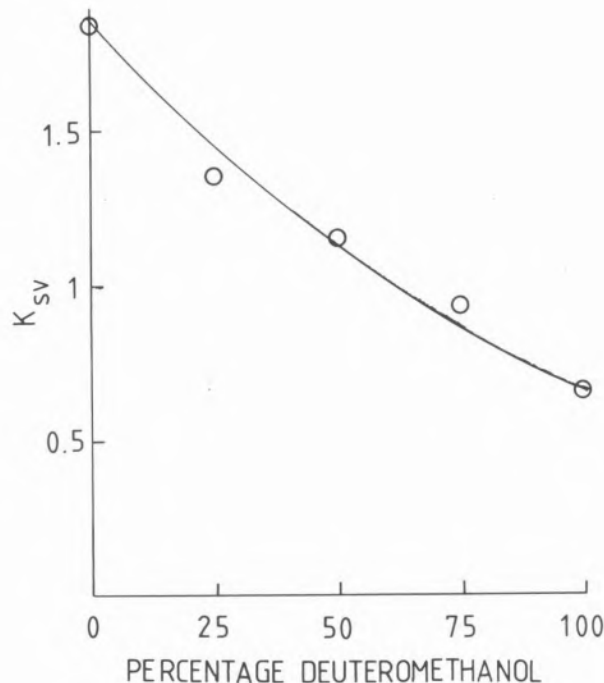


Fig. 2

Stern-Volmer constants for the quenching of the luminescence of uranyl nitrate ($2 \times 10^{-3} M$) in water (pH 4) by methanol-deuteromethanol mixtures as a function of the percentage of deuteromethanol

in the study of such systems, although the scatter in the points shows the method is less sensitive here than with the methanol-isopropanol system.

4 — CONCLUSIONS

The quenching of uranyl luminescence by binary alcohol mixtures would seem to be a reasonably cheap, rapid method for the quantitative analysis of μl quantities of such systems, and clearly also alcohol-water mixtures. The method is suitable for rapid determination of the ratio of protio-to deuterio-alcohols in mixtures. The method has the advantage that it can be easily used in the analysis of volatile compounds which are difficult to study by other methods (e.g.) possessing no suitable absorption spectra). Further, in contrast to many other luminescent systems, it is not necessary to degas solutions of uranyl ion. Finally, the quenching method can be readily automated to make it suitable for batch analysis. Against these advantages we must bear in mind that the method is

not very selective. Interferences are likely, for example, from halide ions [14], transition metal ions [14,15], and ethers [16].

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REFERENCES

- [1] O. STERN, M. VOLMER, *Phys. Z.*, **20**, 183 (1919).
- [2] C. A. PARKER, *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968, p. 493.
- [3] J. BARTOS, M. PESEZ, *Talanta*, **19**, 93 (1972).
- [4] D. A. BRITTON, J. C. GUYON, *Microchem. J.*, **14**, 1 (1969).
- [5] E. SAWICKI, T. W. STANLEY, H. JOHNSON, *Mikrochim. Acta*, 178 (1965).
- [6] R. J. HURTUBISE, *Anal. Chem.*, **48**, 2092 (1976).
- [7] H. B. MARK, Jr, *Talanta*, **19**, 717 (1972).
- [8] E. RABINOWITCH, R. L. BELFORD, *Spectroscopy and Photochemistry of Uranyl Compounds*, Pergamon, Oxford, 1964.
- [9] V. BALZANI, V. CARASSITI, *Photochemistry of Coordination Compounds*, Academic, London, 1970.
- [10] H. D. BURROWS, T. J. KEMP, *Chem. Soc. Rev.*, **3**, 139 (1974).
- [11] See, for example, S. SAKURABA, R. MATSUSHIMA, *Bull. Chem. Soc. Japan*, **43**, 2359 (1970).
- [12] R. J. HILL, T. J. KEMP, (in part) D. M. ALLEN, A. COX, *J. C. S. Faraday I*, **70**, 847 (1974).
- [13] P. BENSON, A. COX, T. J. KEMP, Q. SULTANA, *Chem. Phys. Letts.*, **35**, 195 (1975).
- [14] R. MATSUSHIMA, H. FUJIMORI, S. SAKURABA, *J. C. S. Faraday I*, **70**, 1702 (1974).
- [15] H. D. BURROWS, S. J. FORMOSINHO, M. DA GRAÇA MIGUEL, E. PINTO COELHO, *J.C.S. Faraday I*, **72**, 163 (1976).
- [16] M. AHMAD, A. COX, T. J. KEMP, (in part) Q. SULTANA, *J. C. S. Perkin II*, 1867 (1975).

RESUMO

Aplicações da Supressão de Fluorescência em Análise Quantitativa: A Análise de Misturas de Metanol-Isopropanol e Metanol-Metanol Deuterado pela Supressão da Luminescência do Ião Urânio

A possibilidade de usar a supressão da luminescência do ião urânio na análise de misturas binárias de alcoóis é investigada, e mostra-se que pode fornecer um método barato e rápido para este tipo de análise. O método é adequado para análise de misturas de alcoóis deuterados e não-deuterados, e pode ser adaptado à análise de outras espécies que suprimem a luminescência do ião urânio.