THE USE OF NAPHTHALENE DERIVATIVES IN INORGANIC ANALYSIS

VI. A NEW REAGENT FOR THE FLUORIMETRIC DETECTION OF TIN

by

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INTRODUCTION

The application of the nitro-aminonaphthalene monosulphonic acids[1-3] to the detection and estimation of stannous tin has already been reported in earlier papers of this series. The use of the nitronaphthylamines[4] for the detection of stannous tin has also been described. In this communication a more sensitive reagent, 6-nitro-2-hydroxynaphthalene-8-sulphonic acid is reported for the fluorimetric detection of stannous tin. Using a method previously described[1,3], 55 metallic ions were examined and only stannous tin gave an intense fluorescence when viewed under ultraviolet light, after quenching of any initial fluorescence with $15N$ NH_4OH.

EXPERIMENTAL

Synthesis of reagent

The mononitration of 2-aminonaphthalene-8-sulphonic acid according to the method of FRIEDLANDER AND LUCHT[5] yielded 6-nitro-2-aminonaphthalene-8-sulphonic acid. The ammonium salt (10.0 g) of this acid was diazotised as a paste in water (80 ml) using the "inverted method". Crushed ice (60 g) was added followed by concentrated HCl (14 ml) and the slurry diazotised at 0–5° by the addition of sodium nitrite (3.0 g) in water (20 ml) over a period of 5 min. The mixture was stirred at 0–5° for 2 h after which the precipitated pale yellow diazonium salt was filtered, then added to $2N$ H_2SO_4 (400 ml) and the solution gradually brought to the boil on the hot plate. Boiling was continued until complete evolution of nitrogen ceased and the sulphuric acid solution gave no colour reaction with alkaline phenol. The solution was filtered hot, concentrated on a steam bath, then cooled, the yellow needles of 6-nitro-2-hydroxynaphthalene-8-sulphonic acid being filtered and recrystallised from 50% aqueous alcohol.

The ammonium salt of this acid was prepared by dissolving the free acid in hot 50% aqueous alcohol and neutralizing the solution with ammonium carbonate. The yellow ammonium salt was recrystallised from hot water.

Analysis – Ammonium salt

Calculated for $C_{10}H_{10}O_6N_2S$:	C 41.95; H 3.52; N 9.79.
Found:	C 41.41; H 3.45; N 10.06.

The barium salt was obtained by neutralizing a hot 50% aqueous alcohol solution of the free acid with $BaCO_3$. The solution was filtered hot then cooled, and the orange barium salt which precipitated was re-crystallised from hot water.

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* On study leave at Birkbeck College, University of London (Great Britain).

Analysis – Barium salt

Calculated for $C_{20}H_{12}O_{12}N_2S_2Ba.3H_2O$: C 33.00; H 2.49; Ba 18.88.
Found: C 33.16; H 2.59; Ba 18.95.

Barium was estimated as $BaSO_4$ by digestion of the compound with concentrated sulphuric acid.

6-Nitro-2-hydroxynaphthalene

A solution of 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid (1.0 g) in 10*N* HCl (10 ml) was carefully heated to 160° for 2 h in a sealed glass tube, then cooled. The solution was diluted with H_2O (90 ml), the precipitate (0.48 g) filtered dried and recrystallised from benzene to give pale yellow needles. (M P. 158–9°) This compound showed no depression of melting point when mixed with an authentic sample of 6-nitro-2-hydroxy-naphthalene prepared from 6-nitro-2-amino-naphthalene by a diazotisation procedure*, thus confirming the orientation of the nitro group in the original compound.

Technique of spot testing

The standard procedure reported in previous communications[1,3,4] was used. All fluorescence tests were carried out using a Crompton electric discharge lamp, (125 W, 230/240 V) with a wave length of approximately 3650 Å U V. radiation A 0.1% aqueous solution of the ammonium salt of 6-nitro-2-hydroxynaphthalene-8-sulphonic acid was used as reagent in these tests, the results of which are shown in Table I.

TABLE I

COLOUR AND FLUORESCENCE UNDER ULTRA-VIOLET LIGHT OF SPOTS OF IONS AFTER SPRAYING WITH REAGENT BEFORE AND AFTER TREATMENT WITH 15*N* NH_4OH

Ion	*Before spraying with 15N NH_4OH*	*After spraying with 15N NH_4OH*
[a] Ce^{+4}	Purple	Violet
Fe^{+2}	Brown-violet	Pale brown
Sb^{+3}	Pale purple	Yellow (faint fluorescence)
As^{+3}	Purple	Yellow (faint fluorescence)
As^{+5}	Yellow (faint fluorescence)	Pale violet
W^{+6}	Orange-red	Pale orange-red
Sn^{+2}	Dark purple (faint fluorescence)	Intense blue fluorescence
Fe^{+3}	Brown-violet	Violet-brown
Au^{+3}	Dark violet	Brown
Hg^{+}	Pale violet	Pale brown
Hg^{+2}	Pale violet	Pale brown
Cr^{+6}	Dark violet-brown	Dark violet-brown
Be^{+2}	Yellow (faint fluorescence)	Yellow (faint fluorescence)
Th^{+4}	Faint purple	Pale orange
Bi^{+3}	Pale violet	Yellow (faint fluorescence)
VO_4^{-3}	Red	Red

[a] A freshly prepared aqueous solution of ceric ammonium nitrate (AR grade) was used.

Other ions tested included:

Li^+, Na^+, K^+, Cu^{+2}, Ag^+, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Zn^{+2}, Cd^{+2}, La^{+3}, Pb^{+2}, Mo^{+6}, Te^{+6}, Mn^{+2}, Co^{+2}, Ni^{+2}, Pt^{+2}, Ce^{+3}, VO^{+2}, Cr^{+3}, UO_2^{+2}, Ti^{+4}, Al^{+3}, Ga^{+3}, In^{+3}, Tl^+, Tl^{+3}, Sn^{+4}, Zr^{+4}, Pd^{+2}, Pt^{+4}, VO_3^-, Rb^+, Cs^+, Ti^{+3}, Ru^{+3}, ZrO^{+2}.

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* Authentic sample of 6-nitro-2-hydroxy-naphthalene was kindly supplied by Dr. A. BRYSON, N.S.W. University of Technology, Sydney, Australia.

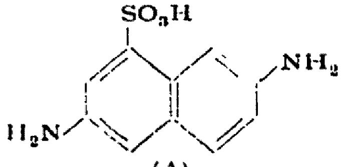
The data in Table I indicate that only Sn^{+2} exhibits intense blue fluorescence under the conditions of test, the remaining ions tabulated yielding coloured spots which were non-fluorescent.

Sensitivity tests

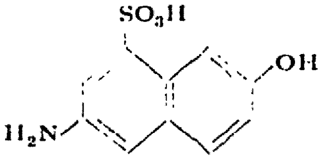
Sensitivity tests for stannous tin were performed using a conventional procedure[1,3,4], a 0.1% aqueous solution of the ammonium salt of 6-nitro-2-aminonaphthalene-8-sulphonic acid being used as a standard reagent[1] for comparative purposes. Using a 0.1% aqueous solution of the ammonium salt of 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid, spots containing 10^{-6} g stannous tin exhibited a blue fluorescence whilst lower concentrations (10^{-7} to 10^{-12} g) gave faintly fluorescent spots, sulphur-yellow in colour. Blank tests performed with a *N* HCl solution and the new reagent, yielded yellow spots with very faint fluorescence. The fluorescence intensity of these blanks was similar to that exhibited by concentrations of stannous tin from 10^{-9} to 10^{-12} g.

DISCUSSION

It has been shown that when 6-nitro-2-aminonaphthalene-8-sulphonic acid is used as a fluorimetric reagent for stannous tin[1,2], the fluorescence can be attributed to the formation of 2,6-diaminonaphthalene-8-sulphonic acid (A).



(A)



(B)

When 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid is used as a reagent in the same test, it is suggested that reduction of the nitro group occurs to yield the corresponding amino-derivative (B) which is the compound responsible for the fluorescence.

Since the substitution of an OH group for an NH_2 group in the original 6-nitro-2-amino-naphthalene-8-sulphonic acid reagent produces a derivative which yields a slightly more sensitive fluorescent test with stannous tin than does the parent compound, it can be said that the contribution of the hydroxyl group to the excited state of (B) is greater than the contribution of the corresponding amino group to the excited state of (A). This result is in keeping with the published observation that the presence of hydroxyl groups in a molecule will enhance the fluorescent properties of that particular compound[6]. Present tests have been limited to those of a qualitative nature but in future experiments, it is hoped to obtain some quantitative information concerning the relative effect of these different substituents in the naphthalene nucleus upon the sensitivity of test.

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SUMMARY

The use of 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid as a new fluorimetric reagent for the detection of tin has been reported. This reagent is capable of detecting 10^{-8} g stannous tin under the conditions of the test and is slightly more sensitive for this purpose than the previously recommended 6-nitro-2-aminonaphthalene-8-sulphonic acid.

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DÉVELOPPEMENT PAR DÉPLACEMENT SUR ÉCHANGEURS D'IONS SÉPARATION DE PLUS DE DEUX IONS

par

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Dans un précédent mémoire[1], nous avons montré que la connaissance de la constante de l'équilibre de deux ions entre une solution et une résine permet de calculer la distance à faire parcourir à une bande contenant les deux corps pour que ceux-ci soient répartis en deux zones jointives. Il est possible de généraliser les résultats obtenus à la séparation d'un nombre quelconque d'ions. Nous envisagerons d'abord le cas de trois corps.

CAS DE TROIS IONS

Fixation des ions sur la résine

On introduit, d'une manière continue, une solution contenant les ions M_1, M_2, M_3 aux concentrations respectives C_1, C_2, C_3 dans une colonne contenant une résine sous forme M_0 de capacité C_R. Nous supposerons que l'affinité des différents ions pour la résine est dans l'ordre: $M_0 < M_1 < M_2 < M_3$. Comment se répartissent les différents ions dans la colonne, lorsqu'une longueur l de résine a été mise en jeu? La partie supérieure de la résine se met en équilibre avec la solution influente et comme M_3 se fixe mieux que M_1 et M_2, il y aura un excès de ces deux ions en tête. Enfin, comme M_2 a plus d'affinité que M_1, il y aura également un excès de M_1 en tête de la zone contenant M_1 et M_2. Les

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