



ELSEVIER

Journal of Chromatography A, 770 (1997) 345–348

JOURNAL OF
CHROMATOGRAPHY A

Short communication

Analysis of sulphonated phthalocyanine dyes by capillary electrophoresis

J. Schofield*, M. Asaf

Department of Colour Chemistry and Dyeing, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK

Abstract

Sulphonated phthalocyanine dyes may be prepared either by direct sulphonation or by mixed condensation methods. Both syntheses will produce mixtures of products. Such mixtures may be analysed by capillary electrophoresis to identify the various degrees of substitution and to indicate the approximate composition of the mixtures.

Keywords: Dyes; Phthalocyanines; Metal phthalocyanines

1. Introduction

In the course of our research many derivatives of phthalocyanine dyes have been prepared. Our especial interest is in zinc phthalocyanine derivatives, but derivatives of copper and cobalt phthalocyanines have been prepared for comparison.

Sulphonated phthalocyanines are of particular interest, both in their own right and as raw materials for preparing other derivatives.

These sulphonated phthalocyanines may be prepared either by direct sulphonation of the unsubstituted parent phthalocyanine or by condensation of sulphonated phthalic acid with urea and a metal salt.

Products with varying degrees of sulphonation may be prepared by varying the sulphonation conditions, or by using mixtures of sulphonated phthalic acid with unsulphonated phthalic anhydride or phthalonitrile in the condensation reaction.

Either method of synthesis will produce mixtures of mono-, di-, tri- and tetra sulphonated products, and for each degree of sulphonation there are several possible positions for the sulphonic acid groups.

Thus there will also be mixtures of geometrical isomers.

Such mixtures are extremely difficult to separate, either for analysis or on a larger scale. Thin-layer chromatography (TLC) will sometimes show the presence of several components but is unreliable due to aggregation effects. Soluble phthalocyanines form aggregates readily in solution and may be disaggregated to differing extents in different solvents [1,2].

What appears to be a single spot on TLC may in fact still be a mixture, and we have often found that a single spot extracted from a TLC plate will split into other components on rerunning the chromatogram.

Some workers have separated sulphonated phthalocyanines by high-performance liquid chromatography (HPLC), [3] but the operating parameters must be very tightly controlled and we have not obtained satisfactory results by this method.

Capillary electrophoresis (CE) has been found to clearly separate sulphonated phthalocyanine mixtures according to the degree of sulphonation. As would be expected, the compounds with the lowest degree of sulphonation have the shortest residence time, and the most highly sulphonated the longest.

*Corresponding author.

As already mentioned, material of each degree of sulphonation will consist of a mixture of geometrical isomers whichever method of synthesis has been used. Commercial sulphophthalic acid is stated to be a mixture of approximately 75% of the 4-sulphonic acid and 25% of the 3-sulphonic acid, so that phthalocyanines prepared from this will contain isomers with the sulpho groups in either position.

In the direct sulphonation of phthalocyanines the entering sulphonic acid group again may enter either position. Thus on each of the benzene rings of a phthalocyanine ring system there are four positions in which a sulphonic acid group may be found.

In the electropherograms of sulphonated phthalocyanines each degree of sulphonation above the first is found to give at least two peaks, more for the higher sulphonic acids, usually only partly separated.

It can be seen that there is a possibility of some interaction possibly by hydrogen bonding, between a sulphonic acid group in the -3 position and the nearest nitrogen atom, while there is much less possibility of such interactions with sulphonic acid groups in the -4 position.

Such interactions would produce variations in charge distribution which might account for the multiple peaks in the electropherogram. Sulphonation in the -3 position is thought to give a more lipophilic product.

The structure of tetrasulpho-zinc phthalocyanine is given in Fig. 1, showing the possible positions of the sulphonic acid groups.

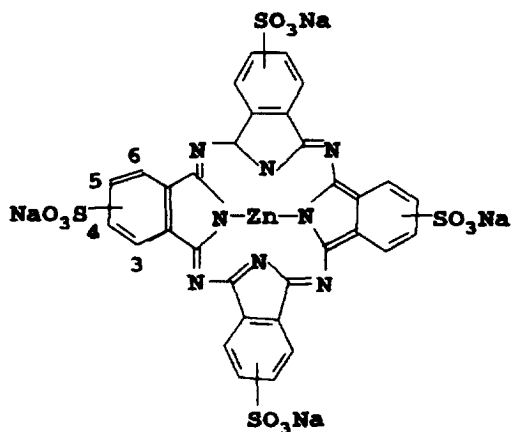


Fig. 1. Structure of zinc phthalocyanine tetrasulphonic acid.

In the disulphonated phthalocyanines there will also be isomers in which the sulphonic acid groups can be either on adjacent or opposite benzene rings. The adjacent structure is claimed to be more hydrophobic than the opposite structure [3].

2. Experimental

2.1. Chemicals

The dye mixtures were synthesised in our laboratory from materials supplied by Sigma (Poole, UK). Commercial dye samples were used without purification.

2.2. Syntheses

Tetrasulphonated phthalocyanines were prepared by a modification of the method of Weber and Busch [4]. The ammonium salt of 4-sulphophthalic acid was reacted with urea and the appropriate metal salt in sulpholane as solvent at 200–210°C.

After cooling, dilution with water and addition of sodium hydroxide to make the sample alkaline, the solutions were filtered and then dialysed to remove inorganic and low-molecular-mass impurities. The products were isolated by vacuum evaporation. Further purification was necessary in some cases. Tetrasulphonated zinc, copper and cobalt phthalocyanines were made by this method.

Mixtures of phthalocyanines sulphonated to various degrees were made by the above method using mixtures of ammonium-4-sulphophthalate with phthalic anhydride in varying proportions, and also by the alternative method of sulphonating the parent phthalocyanine under varying conditions of acid strength, time and temperature.

2.3. Analysis

A Dionex CE system, CES1, (Dionex, Sunnyvale, CA, USA) was used for all analyses. An uncoated fused-silica capillary of 65 cm × 75 μm I.D. was used. The buffer used for almost all the separations was 10 mM potassium dihydrogen phosphate (KH₂PO₄) in deionised water, adjusted if necessary to give a final pH of 9.0.

A 10 mM ammonium acetate buffer adjusted with ammonia to pH 9.4 was tried for some separations, but was found to increase the analysis time without significantly improving resolution. Addition of acetonitrile to the buffer as described by Tapley [5] did not improve resolution in these analyses.

A hydrodynamic injection method was used, with the samples being raised to 50 mm for 10 s. The analyses were run in the constant current mode, generally set at 30 μ A, requiring an average voltage of 28 kV.

Detection was by an on-line UV-Vis detector positioned at the cathode. The detection wavelength was generally set at 630 nm, as the phthalocyanine dyes when aggregated in aqueous solution have a broad absorption in this region.

3. Results

Tetrasulphonated zinc, copper and cobalt phthalocyanines were prepared as described in Section 2.2 and electropherograms were run on their aqueous solutions.

It was at once clear that all three samples gave a group of peaks with approximately the same analysis

time — between 20 and 22 min under the conditions as stated in Section 2.3 (Fig. 2 — zinc phthalocyanine — the other metal complexes give similar results).

Samples of zinc phthalocyanine sulphonated to different extents were then prepared. Sample (A) was prepared by sulphonating zinc phthalocyanine with oleum 20/25% for 6 h at 80°C. An electropherogram of this sample gave a double peak at 10.5 min, a multiple peak at 16–17 min and a very small peak at 21.5 min. Sample (B) was prepared by sulphonating zinc phthalocyanine with oleum 20/25% for 1 h at 60°C. An electropherogram of this sample gave a small peak at 7 min, a double peak at 10.5 min and a very small multiple peak at 17 min.

Mass spectrometric determinations on the solid samples gave indications of the sulphonic acids present, but were not clear as to their proportions. Sample (A) showed a strong signal indicating the disulphonic acid, and a weaker signal indicating the trisulphonic acid. Sample (B) showed a weak signal indicating monosulphonic acid and a stronger signal indicating disulphonic acid. Sample (C) was prepared by the mixed condensation method, using a 5.5:1 ratio of phthalic anhydride to sulphophthalic acid condensed with urea and zinc acetate. An

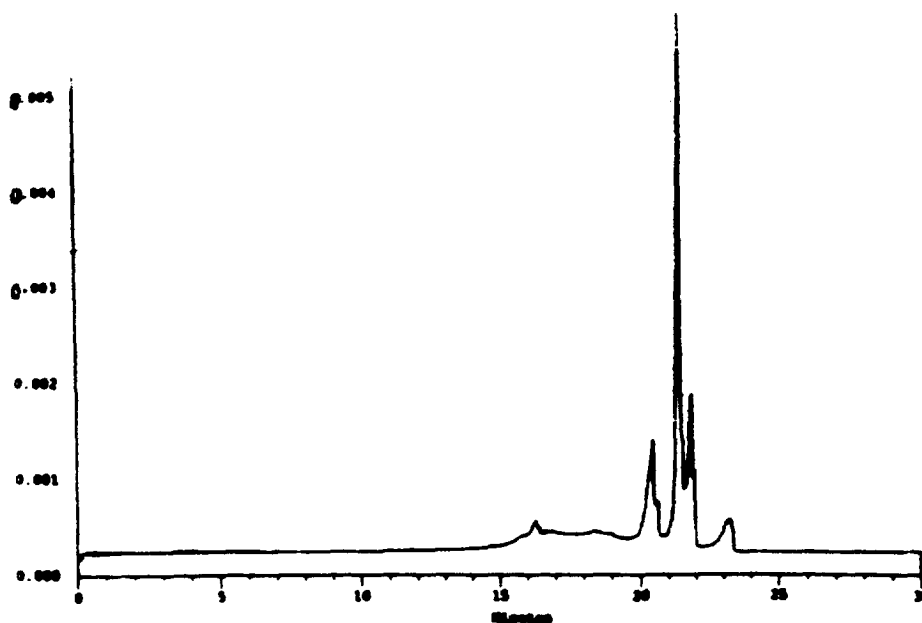


Fig. 2. Electropherogram of zinc phthalocyanine tetrasulphonic acid.

electropherogram of this sample gave a very small peak at 7 min, a sharp peak at 10.5 min and a small multiple peak at 16 min.

Several further samples were prepared using other proportions of sulphophthalic acid to phthalic anhydride, and also by the direct sulphonation method. All showed exactly the same distribution of peaks in their electropherograms.

A sample of chloroaluminium phthalocyanine sulphonyl chloride was next examined. The sample was warmed with dilute sodium hydroxide to hydrolyse the sulphonyl chloride groups to sulphonic acid before running an electropherogram.

A sample was prepared in the laboratory by chlorosulphonation of chloroaluminium phthalocyanine, and a portion of this was again hydrolysed with alkali, before running an electropherogram.

Comparison showed peaks at exactly the same analysis times for both samples but in differing proportions.

Commercial samples of sulphonated copper phthalocyanine dyes showed a large number of peaks, indicating that the dyes were complex mixtures, but the peaks were grouped as described into areas suggesting disulphonic and trisulphonic acids.

This analysis has recently been extended to a zinc phthalocyanine derivative mixture containing carboxylic acid groups, showing a clear separation into four components.

4. Conclusions

CE is capable of analysing mixtures of anionic phthalocyanine derivatives using a phosphate buffer system at pH 9.0. Examples of potential uses of this system include comparison of materials prepared by different methods, following the course of a reaction, checking the purity of dye samples and comparison with standard samples, and monitoring effluents from phthalocyanine dye processes.

Acknowledgments

We would like to thank the Yorkshire Cancer Research Campaign for supporting our work.

References

- [1] K. Bernaur and S. Fallab, *Helv. Chim. Acta*, 44 (1961) 1287.
- [2] J.D. Spikes, *Photochem. Photobiol.*, 43 (1986) 692.
- [3] H. Ali, R. Langlois, J.R. Wagner, N. Brasseur, B. Paquette and J.E. Van Lier, *Photochem. Photobiol.*, 47 (1988) 713.
- [4] J.H. Weber and D.H. Busch, *Inorg. Chem.*, 4 (1965) 469.
- [5] K.N. Tapley, *J. Chromatogr. A*, 706 (1995) 555.