



ELSEVIER

Journal of Chromatography A, 777 (1997) 370–374

JOURNAL OF
CHROMATOGRAPHY A

Short communication

Monitoring the products of condensation of 4-nitrobenzoyl chloride and 2,4-diaminobenzenesulphonic acid by ion-pair high-performance liquid chromatography

Sajid Husain*, R. Narsimha, S. Naseeruddin Alvi, R. Nageswara Rao

Analytical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad-500 007, India

Received 3 December 1996; received in revised form 20 March 1997; accepted 3 April 1997

Abstract

A simple and rapid high-performance liquid chromatographic method for monitoring the process of condensation between 2,4-diaminobenzenesulphonic acid and 4-nitrobenzoyl chloride was developed. The reaction products were separated on a reversed-phase Novapak C₁₈ column using 5 mM tetrabutylammonium hydrogensulphate–acetonitrile (77.5:22.5, v/v) as the eluent. The method was used not only for checking the quality of the condensed products but also for optimization of the process conditions. The method was validated by monitoring several batches of laboratory scale reactions and used successfully for upgrading them to plant level. © 1997 Elsevier Science B.V.

Keywords: Diaminobenzenesulfonic acid; Nitrobenzoyl chloride; Diaminodibenzanilide-4-sulfonic acid; Dyes

1. Introduction

2,4-Diaminobenzenesulphonic acid (2,4DABSA) is an industrially important intermediate in the manufacture of dyes for cotton, wool, leather and cosmetics [1]. It undergoes condensation with cynuric chloride, urethane polymers, etc. to give different colours used in the dye industry [2,3]. Although these processes are well documented in the literature, reports describing its reaction with 4-nitrobenzoyl chloride (4-NBC) are not available.

Our laboratory, in collaboration with an industry producing 2,4-DABSA, has studied the process of the reaction of 2,4-DABSA with 4NBC systematically and optimized the reaction conditions to pro-

duce 4,4''-diaminodibenzanilide-4-sulphonic acid (4,4''DADB4'SA) commercially. While developing the process, HPLC has been used extensively as a technique to monitor products of the reaction.

A thorough literature search has revealed that chemical methods of analysis are generally based on diazotization and coupling [4,5]. But these methods often suffer from interferences and isomerization. Paper and thin-layer chromatographic techniques are quite useful but qualitative in nature [6,7]. HPLC is the technique of choice for separation and quantitation of condensed products of 2,4-DABSA. Cellulose and polystyrene based ion-exchange columns have been used extensively to study the behaviour of aromatic sulphonic acids [8,9]. But the separations on these columns have been found to be affected by the poor recovery of analytes due to strong ad-

*Corresponding author.

sorptions [10]. These problems are generally overcome using ion-pair reagents in reversed-phase liquid chromatography [11,12].

In this paper we describe a simple and rapid ion-pair HPLC method not only for quality assurance but also for process development of the condensed products of 2,4-DABSA acid and 4-NBC.

2. Experimental

2.1. Materials and reagents

All reagents were of analytical-reagent grade unless stated otherwise. Glass-distilled water, HPLC grade acetonitrile (Spectrochem, Bombay, India), tetrabutyl-ammonium hydrogensulphate (TBAHS) (BDH, Poole, UK) and 4-nitrobenzoyl chloride (Lobachemie, Bombay, India) were used. 2,4-DABSA and its condensed products were obtained from M/s. Orchem Intermediates (Hyderabad, India).

2.2. Chromatography

HPLC was performed with a Shimadzu (Kyoto, Japan) LC-6A chromatograph fitted with a 150×3.9 mm I.D., 4 μm C₁₈ Novapak reversed-phase column (Waters, Milford, MA, USA) equipped with a variable-wavelength UV-Vis detector. The detector wavelength was 254 nm for both detection and quantitation. 5 mM aqueous tetrabutylammonium

hydrogensulphate–acetonitrile (77.5:22.5, v/v) was adjusted to pH 4.6 with 5% liquid ammonia and used as mobile phase. The flow-rate was 1.0 ml min⁻¹.

2.3. Procedure

Standard mixtures of 2,4-DABSA, 4-NBC and their derivatives were prepared and diluted with sufficient quantities of mobile phase; 20-μl samples were injected in triplicate by means of Rheodyne (Cotati, CA, USA) Model 7125 valve. Chromatograms and integrated data were recorded with a Chromatopac C-R3A data processing system (Shimadzu, Kyoto, Japan); average values were used for all calculations.

3. Results and discussion

Fig. 1 shows the reactions involved in the process of condensation of 2,4-DABSA and 4-NBC. Initially 1 mole of 4-NBC condenses with 1 mole of 2,4-DABSA to give 4N3'AB4'SA. Later another mole of 4-NBC adds to 4N3'AB4'SA and an intermediate product 4,4''DNDB4'SA is formed. It is then reduced with iron and hydrochloric acid to form 4,4''DADB4'SA. Monitoring the reactions at every step of this process is important not only for accounting the materials but also assuring the quality of the products thus produced. The reactants, intermediates and products of the process were subjected to separation by HPLC. A typical chromatogram of a

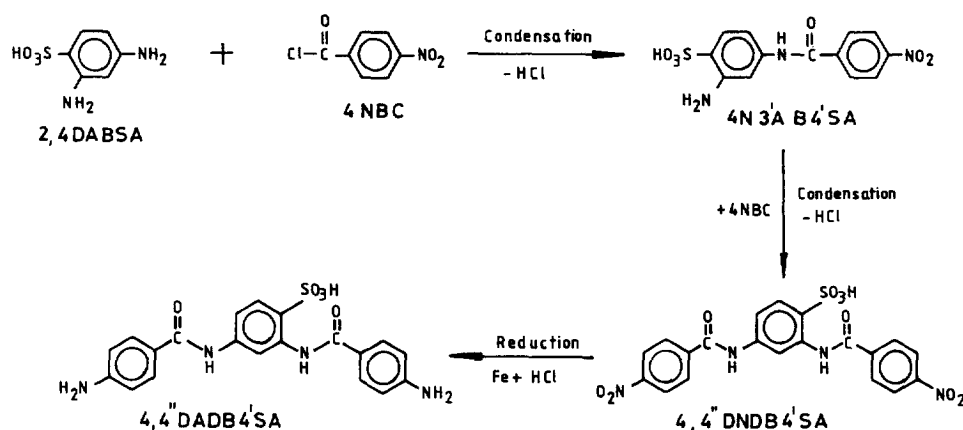


Fig. 1. Reactions followed in preparation of 4,4''DADB4'SA.

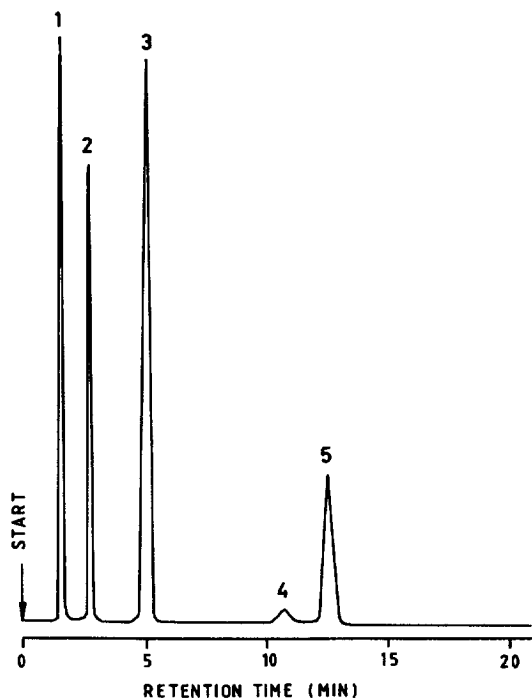


Fig. 2. Chromatogram of a typical mixture containing (1) 2,4-DBSP (10 μg), (2) 4,4''DADB4'SA (9.6 μg), (3) 4-NBC (11.6 μg), (4) 4N3'AB4'SA (10.4 μg), and (5) 4,4''DNDB4'SA (9.6 μg).

mixture is shown in Fig. 2. The peaks were identified by injecting authentic samples. The retention times (t_R), capacity factors (k') and the wavelengths of maximal absorption (λ_{max}) are listed in Table 1.

The effect of concentration of tetrabutylammonium-hydrogensulphate and volume of acetonitrile in the mobile phase has been studied at pH 4.6 systematically. The results are shown in Figs. 3 and 4, respectively. It may be seen from Figs. 3 and 4 that the mobile phase composed of 22.5% acetonitrile

Table 1
Retention data

Compound	Retention time (min)	Capacity factor	λ_{max} (nm)
2,46DABSA	1.44	0.39	220
4,4''DADB4'SA	2.57	1.49	274
4-NBC	5.00	3.85	275
4N3'AB4'SA	10.80	9.48	278
4,4''DNDB4'SA	12.56	11.19	296

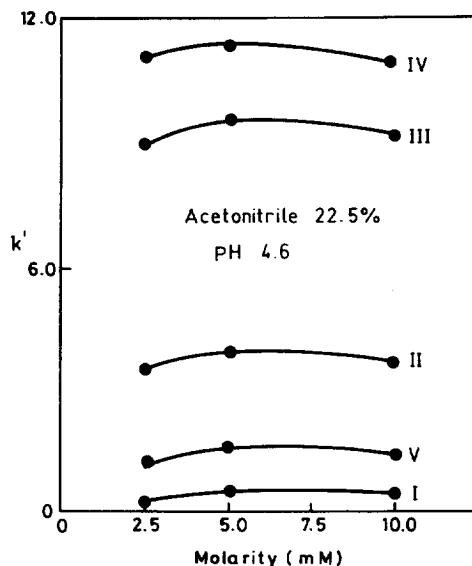


Fig. 3. Effect of concentration of TBAHS on capacity factor (k') of compounds (I) 2,4-DABSA, (II) 4-NBC, (III) 4N3'AB4'SA, (IV) 4,4''DNDB4'SA, and (V) 4,4''DADB4'SA.

trile and 5 mM TBAHS has given optimum separation of the compounds under investigation.

Detector response was determined at two different

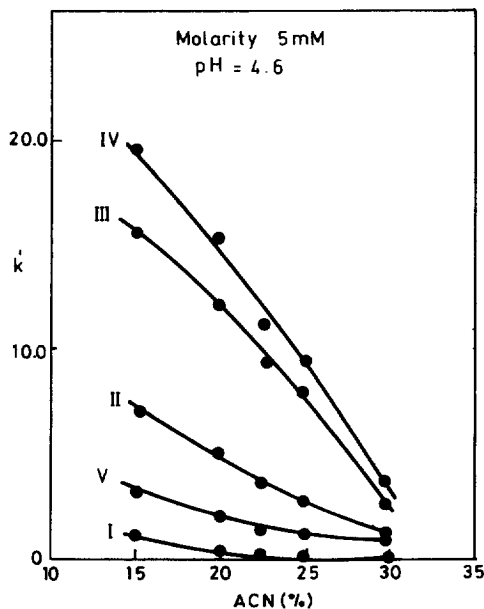


Fig. 4. Effect of acetonitrile (ACN) capacity factor (k') of compounds I, II, III, IV and V.

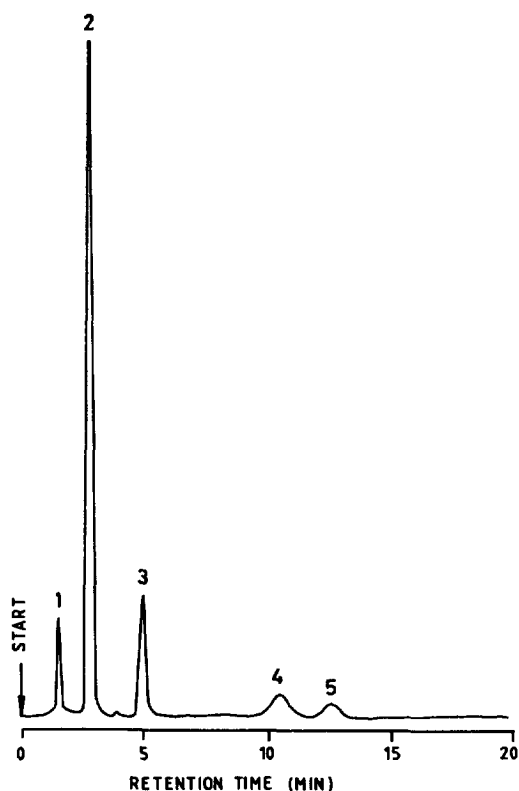


Fig. 5. Chromatogram of a reaction mixture collected after the reduction of 4,4''DNDB4'SA to 4,4''DADB4'SA using Fe and HCl. Peaks: 1=2,4-DABSA, 2=4,4''DADB4'SA, 3=4-NBC, 4=4N3'AB4'SA, 5=4,4''DNDB4'SA.

wavelengths i.e. 254 and 296 nm. The linearity in detector's response for 4,4''DADB4'SA was examined by regression analysis. The correlation coefficients were found to be 0.9994 and 0.9999 respectively.

Samples were collected during the course of condensation between 2,4DABSA and 4NBC and analyzed by HPLC. Fig. 5 shows the HPLC chro-

matogram obtained for a reaction mixture collected after the reduction of 4,4''DNDB4'SA to 4,4''DADB4'SA using Fe and HCl. It may be seen from Fig. 5 that the unreacted 2,4DABSA, 4NBC, 4N3'AB4'SA and 4,4''DNDB4'SA are well separated from 4,4''DADB4'SA and one can determine its purity quite accurately. Three different batches of 4,4''DADB4'SA procured from a local industry were analysed under the same conditions by HPLC. The purity of 4,4''DADB4'SA was found to be a maximum of 92% by HPLC. The contents of 2,4DABSA, 4NBC and other impurities have been determined quantitatively and given in Table 2. It is clear from these results that the method developed is quite simple, rapid and suitable for monitoring the reaction products of 2,4-DABSA and 4-NBC.

4. Conclusion

A simple and rapid ion-pair HPLC method employing a reversed-phase C₁₈ column has been developed for monitoring the condensation products of 2,4-DABSA. It is precise and accurate for the determination of process impurities in the condensed products of DABSA. The method is suitable not only for process development but also for quality assurance of 2,4-DABSA and related products.

References

- [1] K. Venkataraman, in: L.M. Fieser, M. Fieser (Eds.), *The Chemistry of Synthetic Dyes*, Academic Press, New York, 1952, pp. 528–529.
- [2] G. Janina, K. Mirosław, C. Ryszard, N. Waclawa, W. Krystyna, *Pol. PL 126 293* (1985); *C.A.*, 106 (1987) 68730.
- [3] T. Athanassios, A. Peter, H. Paul, *PCT Int. Appl. WO 8 701 123* (1987); *C.A.*, 107 (1987) 79475.

Table 2
Analytical data for condensed products of 2,4-DABSA received from industry

Sample	4,4''DADB4'SA content (%)	Impurities (%)			
		2,4-DABSA	4-NBC	4N3'AB4'SA	4,4''DNDB4'SA
OIPL-1	92.12	0.65	0.62	0.57	6.01
OIPL-2	91.05	0.20	0.54	0.45	6.81
OIPL-3	91.28	0.08	0.52	0.49	6.99

- [4] P.F. Gordon, P. Gregory, *Organic Chemistry in Colour*, Springer-Verlag, New York, 1983, pp. 23–94.
- [5] H. Norwitz, P.N. Keliher, *Talanta* 35 (1986) 311.
- [6] L. Lepri, P.G. Desideri, V. Coas, *J. Chromatogr.* 88 (1974) 331.
- [7] A. Cee, J. Gaspasic, *Mikrochim. Acta*, 1 (1966) 295 CA. 65 (1966) 7983.
- [8] Y. Yoshic, A. Ito, D. Manabe, *Bunseki Kagaku* 26 (1977) 179.
- [9] P. Jandera, J. Churacek, *J. Chromatogr.* 86 (1976) 423.
- [10] K. Obruba, A. Kolonicny, K. Ruzicka, *Chem. Prum.* 26 (1976) 584.
- [11] H. Zou, Y. Zhang, P. Lu, *J. Chromatogr.* 545 (1991) 59.
- [12] P. Jandera, H. Engelhardt, *Chromatographia* 13 (1980) 18.