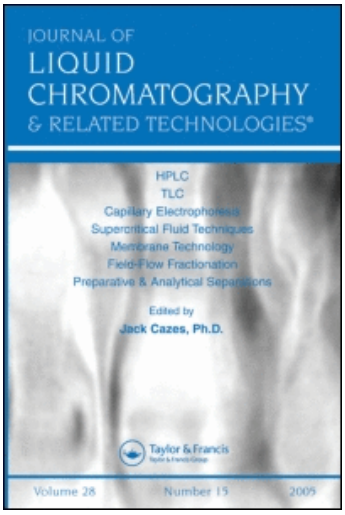

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DETERMINATION OF 4,4′-DIAMINESTILBENE-2,2′-DISULFONIC ACID BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

The quantitative and qualitative determinations of the sodium salt of 4,4′-diaminostilbene-2,2′-disulfonic acid (DASDS) were made using high performance liquid chromatography in the reverse phase system. The determinations were made in samples taken from a reaction mixture which also contained salts of 4,4′-diaminostilbene-2,2′-disulfonic acid (DNSDS) and 4-nitro-4′-aminostilbene-2,2′-disulfonic acid (NASDS). The calibration chart and extensive discussion of the method are presented.

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INTRODUCTION

4,4′-diaminostilbene-2,2′-disulfonic acid (DASDS) is a valuable intermediate product for production of optical whitening agents, which can be applied in paper or textile products to increase their whiteness. Stilbene derivatives are generally used as fluorescent brighteners, and the main raw material for their production is DASDS. Sodium salt of DASDS acid absorbs UV radiation of wavelength 340 nm.

DASDS acid is obtained from 4,4′-dinitrostilbene-2,2′-disulfonic acid (DNSDS) as a result of reduction of nitro to amino groups. On an industrial scale, three methods of DASDS acid production are applied: Beschampe's method, catalytic method, and electrochemical method.[1–4]

In the investigations part of which this study is, the DASDS acid was obtained using the catalytic method. The process comprises two stages: at the first stage 4-nitro-4′-aminostilbene-2,2′-disulfonic acid (NASDS) is produced;[5] next, this acid is further reduced to DASDS acid (Fig. 1).

Structures of DASDS, DNSDS, and NASDS acids are shown in Fig. 2. Separation of these stilbene derivatives was carried out by means of HPLC in the system of reverse phases with a spectrophotometric detector equipped with a diode matrix (DAD), using a column with C_{18} octadecyl packing.

In the well-known literature there is only one reference concerning the determination of stilbene derivates – DNSDS and DASDS. Authors[6] described the qualitative and quantitative analysis by thin layer chromatography (TLC), using $CHCl_3$-DMF mixture as an eluent and densitograph to determine the substance concentration. However, this method is rather time-consuming and the precision is not very high.

The aim of this study was to develop the HPLC method for separation, as well as qualitative and quantitative determination of DASDS acid. Since the reaction mixture may contain DASDS, DNSDS, and NASDS acids whose structures are similar, it may be difficult to estimate the reaction yield, and therefore, it is necessary to develop a proper method of chromatographic analysis.

EXPERIMENTAL

Chemicals and Standard Solutions

Methanol was from J.T. Baker's. Standard DNSDS acid and DASDS, of purity 97%, were from TCI – Tokyo Kusei Organic Chemicals (Japan). The standard NASDS acid is not offered commercially.

NASDS was obtained by column chromatography of samples with a high content of NASDS and separation of the fraction devoid of other admixtures. This fraction was analyzed by the IR method, which confirmed that amino and nitro

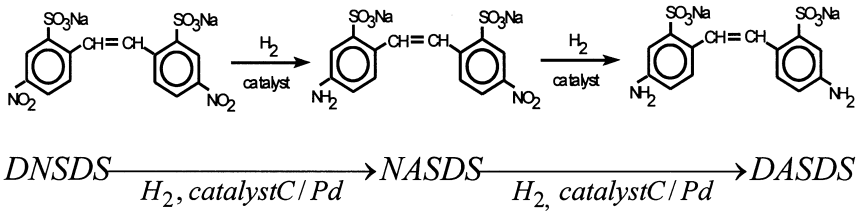

Figure 1. Scheme of synthesis DASDS acid, disodium salt.

groups occurred in parallel in a compound with stilbene acid structure. The final structure of the compound was confirmed by NMR.

Chromatography

The eluent in the analysis of the reaction mass coming from the catalytic reduction of DNSDS acid was a mixture of 500 cm^3 methanol, 485 cm^3 water, and 15 cm^3 TBAP (0.5 M solution of tetrabutylammonium phosphate).

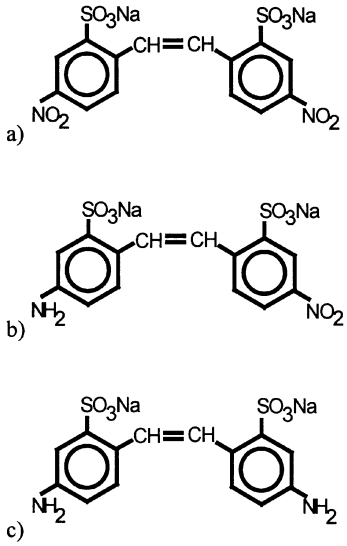

Figure 2. Structures of the compounds studied: a) 4,4′-dinitrostilbene-2,2′-disulfonic acid, disodium salt (DNSDS); b) 4-nitro-4′-aminostilbene-2,2′-disulfonic acid, disodium salt(NASDS); c) 4,4′-diaminostilbene-2,2′-disulfonic acid, disodium salt (DASDS).

An LC 250 type liquid chromatograph with a 235C type DAD detector (Perkin-Elmer, USA) was used for the analyses. A standard chromatographic column C_{18} (Altech, UK) (for the reverse phase, octadecyl) 250 mm × 4 mm of I.D. with packing grain diameter equal to 5 μm was used.

The eluent flow rate through the column was about 1 $cm^3\,min^{-1}$, at the pressure of about 10 MPa. The analyses were performed in the isocratic system. Chromatograms of samples coming from the investigations of catalytic reduction of DNSDS acid were recorded at a wavelength $\lambda = 350$ nm, at which maximum absorbency for DNSDS and DASDS acid occurred. This maximum was found when making absorption spectra of aqueous solutions of DNSDS and DASDS acid in a Lambda 10 spectrophotometer (Perkin-Elmer) (Fig. 3).

Preparation of Standard Substance Samples for Analysis

A weighed sample ca. 0.1000 g of the tested standard substance, in the form of paste or powder, was dissolved in distilled water and transferred quantitatively to the measuring flask 50 cm^3 in volume and completed with distilled water. Next, dilutions necessary to prepare an analytical curve were made. To make standard solutions, the standard substances described above were used.

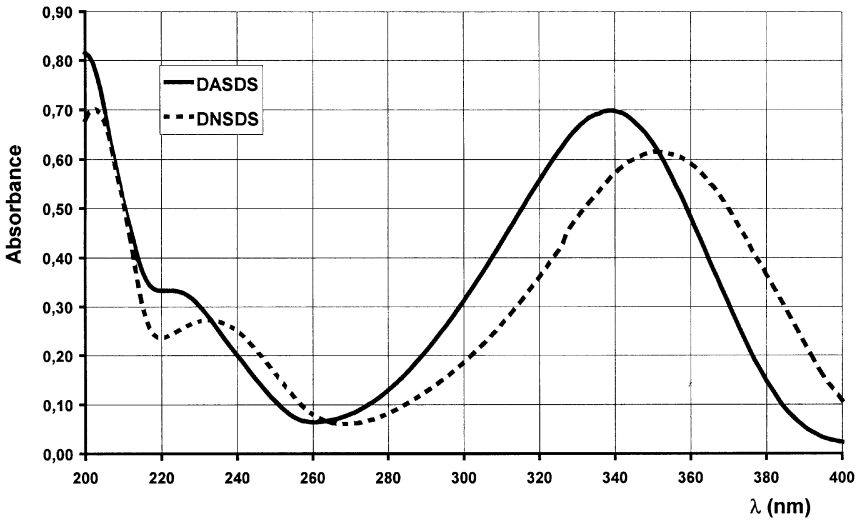

Figure 3. Absorption spectra of aqueous solutions of DNSDS and DASDS acids.

Analytical curve of the chromatographic determination of DNSDS acid is expressed by the equation (peak integration vs concentration)

$$y = 1.54775 \times 10^9 \times x$$

Coefficients were obtained with following parameters:

correlation coefficient = 0.98904
standard deviation = 2.04644×10^6
number of data points = 5
range of peak integration = $0 \div 3 \times 10^7$
range of concentration = $0.000 \div 0.020\ \text{mgdm}^{-3}$

Analytical curve of the chromatographic determination of DASDS acid is expressed by the equation (peak integration vs concentration)

$$y = 1.11998 \times 10^5 \times x$$

Coefficients were obtained with following parameters:

correlation coefficient = 0.99964
standard deviation = 2.86985×10^5
number of data points = 5
range of peak integration = $0 \div 2.4 \times 10^7$
range of concentration = $0.000 \div 0.020\ \text{mgdm}^{-3}$

RESULTS AND DISCUSSION

During DASDS acid production by the catalytic reduction method, a reaction mixture may contain unreacted DNSDS and NASDS acids whose presence is a result of partial reduction of DNSDS acid.

Samples for analysis were taken directly from the reactor in which PNTS acid was oxidized. A 1–2 cm^3 sample of the reaction solution was taken from the reactor, and then from this sample 0.5 cm^3 of the solution, was transferred by a pipette to a measuring flask 50 cm^3 in volume, which contained about 25 cm^3 of distilled water (to stop the chemical reactions). Next the flask was completed with distilled water.

This prepared solution was injected into the chromatographic column by a metering valve of capacity 20 μL. Standard solutions and sample solutions were injected, subsequently, to the column front. For each experiment, the concentration of DNSDS and DASDS in the reaction mass was investigated as the chemical reaction proceeded. In none of the samples, was the presence of DADBZ found.

Retention times for particular components were as follows:

DASDS acid – 3.19 min
DNSDS acid – 12.37 min

The heights of chromatographic peaks obtained were proportional to the concentration of a given component in the solution. Using the previously determined calibration curves for all components, their content in the reaction mass in particular samples was specified. An example of the chromatogram of the reaction mass sample is shown in Fig. 4.

Sensitivity and Accuracy of the Method

It was found, experimentally, that the sensitivity and accuracy of the proposed analytical method was about 0.1%. An increase of weighed sample, and concentration of the sample solutions, enables a detection of 0.001% and determination of 0.01% pollutants present in the samples.

To estimate the error of the method, the following two experiments were performed. The standard solution of DNSDS was injected ten times and its height was measured. It was observed, that the scatter did not exceed 1%. Next, six subsequent samples of DNSDS solution taken from separate weighed samples were injected. The calculated scatter was lesser than 1%.

The error of the method was caused mainly by an error of the chromatographic process. According to the service manual, repeatability of injecting the metering valve is not higher than 1%. The error of the method is higher when samples are injected by micro-syringes.

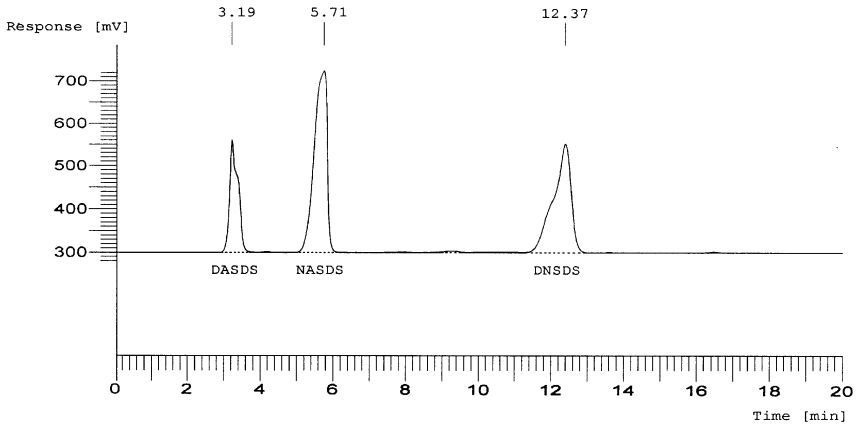

Figure 4. A chromatogram of the reaction mass sample during catalytic reduction of 4,4′-dinitrostilbene-2,2′-disulfonic acid. The curve illustrates solution absorbency at the wavelength $\lambda = 350\,\text{nm}$.

CONCLUSIONS

A method for qualitative and quantitative analysis of the reaction mass coming from the catalytic reduction of DNSDS acid was proposed. High performance liquid chromatography (HPLC) was applied. Investigations were carried out using an LC 250 DAD detector (Perkin-Elmer) and a standard C_{18} column for phase separation in the reverse phase system. The eluent was a water-methanol system with TBAP added. Very good accuracy and repeatability of the analysis was achieved, which enabled the application of DNSDS and DASDS determination in the reaction mass samples in the identification of the catalytic reduction kinetics. The short time of the analysis (about 15–20 min.) is an additional advantage of the proposed analytical method.

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