

**SPECTROPHOTOMETRIC AND PAPER CHROMATOGRAPHIC ANALYSIS  
OF MIXTURES OF 4-NITROTOLUENE-2-SULPHONIC ACID  
AND 4,4'-DINITROSTILBENE-2,2'-DISULPHONIC ACID\***

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Mixtures of 4-nitrotoluene-2-sulphonic and 4,4'-dinitrostilbene-2,2'-disulphonic acids were analyzed by a direct spectrophotometric method and by a method consisting of their paper chromatographic separation and d.c. polarographic or spectrophotometric determination.

The ever-increasing production of optical brightening agents based on diaminostilbene has stimulated an increased demand for methods for the analysis of the corresponding starting substances and intermediates<sup>1-5</sup>. The concern of the present work is the analysis of mixtures of 4-nitrotoluene-2-sulphonic acid (NTS) and 4,4'-dinitrostilbene-2,2'-disulphonic acid (DNS), which are formed during the production of 4,4'-diaminostilbene-2,2'-disulphonic acid. Attention is first paid to the direct spectrophotometric determination based on the differences in the UV spectra of the two acids, stress being laid on the determination of small quantities of NTS in the presence of DNS as the major component. Since the industrial samples may contain other impurities as well, combined methods of their spectrophotometric or polarographic determination following their paper chromatographic separation are also worked out.

**EXPERIMENTAL**

**Reagents and Apparatus**

Stock solutions of NTS and DNS in distilled water were prepared in a concentration of 10 mmol . l<sup>-1</sup> and standardized titanometrically<sup>1-4</sup>. Paper chromatographic separations were performed on Whatman 3 paper using an n-butanol-acetic acid-water 4 : 1 : 5 mixture as the eluting agent. The polarographic measurements were performed on an LP 7e polarograph interfaced to a TZ 213 s line recorder (both Laboratorní přístroje, Prague), the spectrophotometric measurements were carried out on a Specord UV-VIS instrument (Carl Zeiss, Jena) using 0.5 and 1 cm quartz cells.

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### Procedures

*Direct spectrophotometric determination of NTS and DNS.* Solutions of the individual substances in concentrations of  $5 \mu\text{mol l}^{-1}$  to  $1.5 \text{ mmol l}^{-1}$  were prepared and their spectra were recorded over the region of  $40\,000$ – $28\,000 \text{ cm}^{-1}$ . Solutions containing the two substances in various proportions were also measured.

*Spectrophotometric determination of NTS and DNS following their paper chromatographic separation.* The mixture to be separated by paper chromatography was applied to the start in a volume of  $200 \mu\text{l}$ . The developed chromatographic bands detected under a UV lamp were cut out and eluted with  $3 \times 25 \text{ ml}$  of water at room temperature; the eluates were filtered over an S3 glass filter into  $100 \text{ ml}$  volumetric flasks, diluted to volume, and their UV spectra were immediately measured. The analytical wavenumbers for NTS and DNS were  $36\,000$  and  $28\,000 \text{ cm}^{-1}$ , respectively. The calibration curve for the two substances was plotted by using samples containing  $50$ ,  $100$ ,  $150$ , and  $200 \mu\text{l}$  of NTS solution ( $40 \text{ mmol l}^{-1}$ ) or DNS solution ( $20 \text{ mmol l}^{-1}$ ) in  $100 \text{ ml}$ . In view of the effect of light<sup>6</sup>, the chromatographic treatment was performed and the solutions were kept in darkness.

*Polarographic determination of NTS and DNS following their paper chromatographic separation.* The separation was performed as above, only Britton–Robinson buffers pH 5 and pH 10 were used for the elution of the spots of NTS and DNS, respectively. The eluates filtered over an S3 glass filter into  $100 \text{ ml}$  volumetric flasks were diluted to volume with the respective buffers. Eight ml of the solution was placed in a polarographic vessel after Novák and  $0.1 \text{ ml}$  of  $0.5\%$  gelatine solution was added. The polarographic waves were recorded after a  $5 \text{ min}$  nitrogen purging. The calibration curve was plotted using solutions in concentrations as above, Britton–Robinson buffers of the corresponding pH serving as solvents.

### RESULTS AND DISCUSSION

The UV spectra of the two substances are shown in Fig. 1. The calibration plots for the determination of NTS at  $36\,000 \text{ cm}^{-1}$  and DNS at  $28\,000 \text{ cm}^{-1}$  are linear

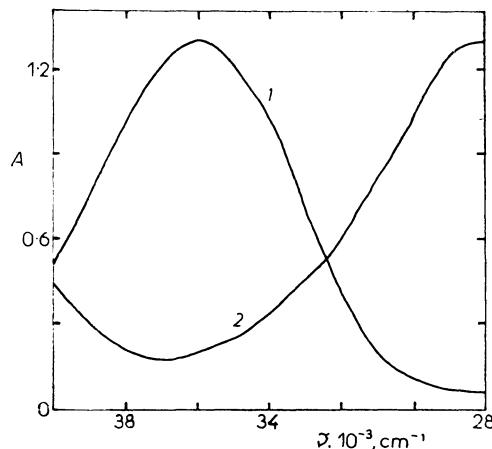


FIG. 1  
Absorption spectra of NTS,  $c = 0.16 \text{ mmol l}^{-1}$  1, and DNS,  $c = 0.05 \text{ mmol l}^{-1}$  2; optical path length 1 cm

over the concentration region of  $5 \mu\text{mol l}^{-1}$  to  $0.2 \text{ mmol l}^{-1}$ . The molar absorptivities, as obtained by linear regression treatment for NTS at  $36\,000 \text{ cm}^{-1}$  and DNS at  $28\,000 \text{ cm}^{-1}$  are  $0.840 \cdot 10^4$  and  $2.60 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ , respectively; the molar absorptivities of NTS at  $28\,000 \text{ cm}^{-1}$  and of DNS at  $36\,000 \text{ cm}^{-1}$  are  $0.025 \cdot 10^4$  and  $0.400 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ , respectively. Zero intercepts were obtained; the correlation coefficients lay within the  $0.9997 - 0.9993$  range.

Thus the concentrations of the substances can be calculated by solving the system of equations

$$A_{28} = (\varepsilon_{\text{NTS}})_{28} c_{\text{NTS}} + (\varepsilon_{\text{DNS}})_{28} c_{\text{DNS}}$$

$$A_{36} = (\varepsilon_{\text{NTS}})_{36} c_{\text{NTS}} + (\varepsilon_{\text{DNS}})_{36} c_{\text{DNS}}$$

TABLE I

Direct spectrophotometric analysis of mixtures of NTS with DNS; optical path length 1 cm

Added, mg		Found <sup>a</sup> , mg		Relative standard deviation, mg	
NTS	DNS	NTS	DNS	NTS	DNS
4.32	18.97	4.54	19.31	0.08	0.20
8.65	14.23	8.93	14.56	0.20	0.21
12.97	9.49	13.25	9.72	0.23	0.14
2.16	4.74	2.11	4.89	0.09	0.15
4.32	4.74	4.32	4.89	0.11	0.13
8.65	4.74	8.32	4.89	0.16	0.15
12.97	4.74	12.77	4.89	0.21	0.11
17.30	4.74	16.91	4.89	0.20	0.14
21.62	4.74	21.27	4.89	0.19	0.09
2.16	23.97	2.31	23.67	0.09	0.19
4.32	23.97	4.47	23.67	0.12	0.21
8.65	23.97	8.69	23.67	0.15	0.24
12.97	23.97	12.97	24.05	0.14	0.20
17.30	23.97	16.91	24.05	0.17	0.23
21.62	23.97	21.01	24.05	0.23	0.19
2.16 <sup>b</sup>	47.44	1.99	47.91	0.07	0.32
4.32 <sup>b</sup>	47.44	4.04	47.91	0.11	0.29
8.65 <sup>b</sup>	47.44	8.67	47.91	0.13	0.21
12.97 <sup>b</sup>	47.44	12.77	47.91	0.14	0.22
17.30 <sup>b</sup>	47.44	16.91	47.91	0.16	0.28
21.62 <sup>b</sup>	47.44	21.02	47.91	0.19	0.26

<sup>a</sup> Average of five determinations, from which the relative standard deviation was also calculated;  
<sup>b</sup> optical path length 0.5 cm.

where  $A$ 's are absorbances,  $e$ 's are the absorptivities of the two substances, and the subscripts 28 and 36 refer to the wavenumbers of 28 000 and 36 000  $\text{cm}^{-1}$ , respectively. The results of analyses so performed are given in Table I; with the NTS-to-DNS weight ratios of 5 : 1 to 1 : 25 the error of determination of NTS and of DNS is below 5% rel. and 3% rel., respectively.

For the paper chromatographic separation the n-butanol-acetic acid-water mixture was chosen with regard to the published data for aromatic sulpho acids<sup>7</sup> and optical brightening agents based on 4,4'-diaminostilbene-2,2'-disulphonic acid<sup>8</sup>; the  $R_F$  values for NTS and DNS were 0.66 and 0.48, respectively. The spectra have to be measured immediately after the elution because the absorbance of DNS de-

TABLE II

Spectrophotometric determination on NTS and DNS following the paper chromatographic separation of their mixture

Added, mg		Found <sup>a</sup> , mg		Relative standard deviation, mg	
NTS	DNS	NTS	DNS	NTS	DNS
0.501	1.899	0.471	1.741	0.02	0.12
1.013	1.424	0.993	1.382	0.04	0.08
1.520	0.949	1.389	0.903	0.10	0.04
2.026	0.475	1.913	0.475	0.13	0.002

<sup>a</sup> Average of five determinations, from which the relative standard deviation was also calculated.

TABLE III

Polarographic determination of NTS and DNS following the paper chromatographic separation of their mixture

Added, mg		Found <sup>a</sup> , mg		Relative standard deviation, mg	
NTS	DNS	NTS	DNS	NTS	DNS
0.507	1.899	0.495	1.848	0.02	0.10
1.013	1.424	1.013	1.439	0.02	0.06
1.520	0.949	1.398	0.936	0.08	0.03
2.026	0.475	1.874	0.459	0.11	0.02

<sup>a</sup> Average of five determinations, from which the relative standard deviation was also calculated.

creases with time, presumably due to its *cis-trans* isomerization. The results of determinations so performed are given in Table II; for mixtures containing 0.5–2.0 mg of the two acids, the relative error of their determination does not exceed 10%, which is reasonable for such amounts of analyte and for the technique used.

The polarographic waves were best developed in Britton–Robinson buffer solutions at pH 5 for NTS (ref.<sup>4</sup>) and at pH 10 for DNS (ref.<sup>1</sup>), and these buffers were used for the extraction of the spots after the paper chromatographic separation. The wave height for DNS was constant<sup>6</sup> even where the absorbance decreased considerably. The results of analyses so performed are given in Table III; again, for mixtures of 0.5–2 mg of the two acids, the relative error of determination is lower than 10%.

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