POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF 4,4′-BIS[(4-PHENYLAMINO-6-MORPHOLINO-1,3,5-TRIAZIN-2-YL)-AMINO]STILBENE-2,2′-DISULFONIC ACID

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The polarographic and voltammetric behaviour of the title compound, which is the basic component in many commercial optical whitening agents, was investigated. The optimum conditions were found for the determination of the substance in dimethylformamide solutions containing 5% (v/v) water by tast polarography, differential pulse polarography, linear sweep voltammetry using a hanging mercury drop electrode, and differential pulse polarography using a hanging mercury drop electrode over the concentration regions of 100–500, 10–500, 10–500, and 1–100 μmol l^{-1}, respectively. Practical applicability of the newly developed methods to the determination of the analyte in technical products, either direct or following separation by thin layer chromatography, was verified.

4,4′-Bis[(4-phenylamino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2′-disulfonic acid (PMASDA) is the basic component in many commercial optical whitening agents, such as Blankophor MBBH (Bayer, Leverkusen, Germany) and Rylux D (VCHZ Synthesia, Pardubice, Czech Republic). This substance is used in the textile and paper industries and in the manufacture of washing agents and synthetic fibres. Optical whitening agents of this kind are employed during the whitening of cellulose and animal as well as polyamide fibres. Their analysis is of importance from the product quality control and wastewater control aspects because such water pollutants emerge from households, laundries, and the textile and paper industries[1]. Compounds of this type are usually not regarded as hazardous to human health[1,2] but some publications suggest that special attention should be paid to diaminostilbene derivatives with regard to their potential mutagenity, although their carcinogenic effects are not demonstrable[3].

A detailed overview of titrimetric, spectrometric and separation methods applicable to the analysis of this type of compounds can be found in our preceding paper[4]. As yet, polarography has not been used for the determination of PMASDA, apparently due to the reluctant polarographic reduction of both the stilbene C=C bond and the triazine

ring. The review mentioned[4] suggests that only media with high concentrations of organic solvents that are difficult to reduce are feasible for the polarographic quantitation of PMASDA. This is so because stilbene derivatives exhibit waves with half-wave potentials $E_{1/2}$ lying typically within the region of –2.1 to –2.8 V vs SCE, in dependence on medium. The effect of substituents on the half-wave potential of polarographic reduction of stilbene derivatives has been the concern of paper[5]. As suggested in ref.[6], the surroundings of the double bond do not affect the $E_{1/2}$ value appreciably. A highly negative potential is rather disadvantageous from the polarographic point of view, particularly if substances in complex matrices are to be determined. Aqueous solutions have only been used during the study of adsorption of some derivatives of 4,4′-bis(triazinylamino)stilbene-2,2′-disulfonic acid by AC polarography and oscillopolarography[7–10]. Dimethylformamide proved to suit well to the investigation of the mechanism of polarographic reduction of stilbene and its derivatives[11,12].

Based on knowledge acquired during the development of polarographic and voltammetric methods of determination of the structurally related 4,4′-bis[(4-phenylamino-6-methoxy-1,3,5-triazin-2-yl)amino]stilbene-2,2′-disulfonic acid[4], solution of tetraethylammonium bromide in dimethylformamide containing 5% (v/v) water, which enables sufficiently negative potentials for the polarographic reduction of the stilbene C=C bond to be reached, was employed in this work as the supporting electrolyte. The polarographic behaviour of PMASDA in such solutions was studied by tast polarography, differential pulse polarography (DPP) using a conventional dropping mercury electrode (DME), linear sweep voltammetry (LSV), and differential pulse voltammetry (DPV) using a hanging mercury drop electrode (HMDE).

EXPERIMENTAL

Reagents

PMASDA disodium salt ($C_{40}H_{30}N_{12}S_2O_8Na_2$, see formula *I* in Scheme 1; CAS Name: 2,2′-(1,2-ethenediyl)bis[5-[(4-(4-morpholinyl)-6-phenylamino)-1,3,5-triazin-2-yl]amino]benzenesulfonic acid, disodium salt; CAS Registry Number: 16090-02-1) was obtained by double recrystallization of the technical product Blankophor MBBH (Bayer, Leverkusen, Germany) from water–methanol (1 : 1) mixed solutions. A stock solution of the compound in dimethylformamide at a concentration of 1 mmol l^{-1} was prepared by dissolving 0.9168 g of the substance and diluting to 1 litre. More dilute solutions were prepared by diluting the stock solution with dimethylformamide. Stock solution of the substance in methanol was prepared likewise. The purity and active content of the chemicals were checked by oxidimetric and precipitation titrations, thin layer chromatography and spectrophotometric measurements (see later). In order to prevent *cis–trans* isomerization, all solutions were prepared, diluted and stored in darkness, and measurements were performed in brown glass vessels.

Dimethylformamide (pure, Lachema Brno, Czech Republic) was multiply distilled in the presence of potassium hydroxide prior to use[13]. Tetraethylammonium bromide (pure, Lachema Brno, Czech Republic) was recrystallized from a water–methanol (1 : 1) mixed solvent.

The titrimetric determination was carried out by using Septonex ([1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide; purity as per PhBS 4, Slovakofarma Hlohovec, Slovak Republic) and sodium lauryl sulfate of reagent grade purity (Lachema Brno, Czech Republic).

Water was redistilled in a quartz still. All the remaining chemicals used were of reagent grade purity (Lachema Brno, Czech Republic).

Apparatus

A PA4 polarographic analyzer interfaced to an XY 4105 recorder (both Laboratorni pristroje, Prague, Czech Republic) was used in the three-electrode connection with a platinum sheet auxiliary electrode. A silver chloride electrode served as the reference electrode, connected to the polarographed solution by a salt bridge containing tetraethylammonium bromide (0.1 mol l^{-1}) in dimethylformamide. To enable comparison with other data, the potentials were related to the saturated calomel electrode (SCE). Either a conventional dropping mercury electrode with a capillary giving a rather long drop time (for tast polarography and DPP) or an SMDE 1 static mercury drop electrode (Laboratorni pristroje, Prague, Czech Republic) in the HMDE mode was employed as the working electrode.

The DME reservoir height was 25 cm, the drop time at 0 V in 0.1 mol l^{-1} potassium chloride was 8.91 s, and the mass flow rate was 0.38 mg s^{-1}. The HMDE capillary diameter was 0.138 mm and the largest possible drop was used (valve opened for 160 ms). Unless stated otherwise, the following experimental setting was used in the polarographic or voltammetric measurement: potential sweep rate 5 mV s^{-1} (tast, DPP) or 20 mV s^{-1} (LSV, DPV), electronically controlled drop time 1 s, pulse height –50 mV (DPP) or –25 mV (DPV).

Oxygen was removed from the solutions by nitrogen purging; nitrogen was purified by passing it through a solution of chromium(II) ions in dilute hydrochloric acid (1 : 1) over a zinc amalgam. Furthermore, before entering the electrochemical vessel, the nitrogen was passed through a solution of the same composition as the solution polarographed.

Absorption spectra were measured on a Pye Unicam 8800 UV/VIS spectrophotometer (Philips, Cambridge, U.K.) using quartz cells 1 or 2 cm optical pathlength.

Oxidimetric potentiometric titrations of the magnetically stirred solutions were performed by using an OP 208/1 pH-meter (Radelkis, Budapest, Hungary) equipped with a platinum wire indicator electrode and a saturated calomel reference electrode. Precipitation titrations were carried out by means of a Spekol 11 instrument equipped with a Model Ti titration attachment (Zeiss, Jena, Germany) fitted with an electromagnetic stirrer, using cells 30 ml in volume; wavelength 700 nm.

Thin layer chromatography was conducted with a commercial set on Silufol UV 254 plates (Kavalier, Votice, Czech Republic).

An M 415 centrifuge (Chirana, Czech Republic) and a Model 350 rotary vacuum evaporator (Unipan, Poland) were employed during the purification and separation operations.

All measurements were conducted at room temperature.

Procedures

For the polarographic and voltammetric measurements, 1.00 ml of a tetraethylammonium bromide solution in dimethylformamide (c = 0.1 mol l^{-1}), 0.5 ml of water, and an appropriate volume of the PMASDA solution in dimethylformamide were added to a 10 ml volumetric flask and diluted to volume with dimethylformamide. Oxygen was removed by nitrogen purging for 10 min, and the polarographic or voltammetric curve was recorded. Calibration curves were measured in triplicate and subjected to linear regression treatment by the least squares method. The limit of determination L_Q was calculated as tenfold the standard deviation for 7 analyte determinations at the concentration corresponding to the lowest point of the calibration curve[14].

Oxidimetric determination of PMASDA in the preparations was based on the method[15] where the stilbene double bond is oxidized with permanganate to give 2 molecules of the corresponding aldehyde. The procedure was as follows: Precisely 100 mg of sample were dissolved in 50 ml of redistilled water, and 0.5 g of each of sodium chloride and sodium hydrogen carbonate were added. The mixture was titrated with a 0.033 mol l^{-1} potassium permanganate solution using potentiometric control with a platinum indicator electrode and a saturated calomel reference electrode. The potential established rather slowly, and therefore the titration curve points were read 2 min after titrant addition. The procedure was conducted at room temperature. One ml of the titrimetric solution, whose titre was determined by titration of oxalic acid in sulfuric acid solution[16], corresponded to 0.0230 g PMASDA.

Septonex served as the titrimetric solution for the precipitation titrations, where 1 molecule of PMASDA reacted with 2 molecules of Septonex[17]. The procedure was as follows: An amount of 0.075 g of sample was dissolved in a water–ethanol (2 : 1) mixture and diluted with this mixture to 500 ml. A volume of 20 ml of this solution in a 30 ml cell was titrated with 0.0065 mol l^{-1} Septonex solution (2.8 g Septonex in a litre). The end point was determined turbidimetrically at a wavelength of 700 nm, chosen with respect to the fluorescence and absorption patterns of PMASDA. One ml of the titrimetric solution, standardized by two-phase precipitation titration of sodium lauryl sulfate[17] using an acid mixture of dimidium bromide and disulfine blue (2 : 1) as the indicator, corresponded to 2.979 mg of PMASDA.

For the quantitation of PMASDA in the commercial products, a precisely weighed amount of sample (about 100 mg) was dissolved with dimethylformamide in a 50 ml volumetric flask and diluted with this solvent to volume. One ml of the solution was mixed with 1 ml of 0.01 mol l^{-1} tetraethylammonium bromide solution in dimethylformamide and 0.5 ml of redistilled water, and the whole was diluted to 10 ml with dimethylformamide. The tast or DP polarogram was recorded after nitrogen purging. The analyte content was determined by using a calibration curve obtained with the pure compound.

When checking the purity of the chemicals by TLC, a volume of 10 μl of a 1 mmol l^{-1} PMASDA solution in dimethylformamide was applied to the start and the solvent was evaporated with a warm air stream. The ascending mode was used. All work, from the solution preparation to the developed chromatogram drying, was accomplished in a dark room. Detection consisted in a short exposure to UV radiation. The following mobile phases were employed: methanol–ammonia–water (10 : 4 : 1; R_F 0.83), methanol–chloroform–ammonia (7 : 8 : 2 and 7 : 12 : 2; R_F 0.79 and 0.64, respectively), acetone–benzene–water–ammonia–tetrabutylammonium iodide (0.1 mol l^{-1}) (70 : 20 : 7 : 4 : 2; R_F 0.61), and benzene–dioxane–methanol–ammonia (5 : 4 : 2 : 1; R_F 0.28). The purified preparation exhibited a single spot in all tests.

The procedure for TLC separation of PMASDA from the technical products was as follows: An amount of 100 mg of sample was dissolved in 10 ml of methanol, and an 50 μl aliquot was applied to the start. Development proceeded in the ascending mode using saturated vapours of the methanol–chloroform–ammonia (7 : 12 : 2) mobile phase. The chromatogram was dried and the spot detected by exposure to UV radiation, and a rectangle about 1.5 × 3.5 cm containing the spot was cut out, tapered, and suspended in a dish containing the methanol–ammonia (4 : 1) eluting mixture, with which the spot was washed directly into the polarographic vessel. The solvent was removed by evaporation in a warm air stream, the residue was dissolved in a 0.001 mol l^{-1} tetraethylammonium bromide solution in dimethylformamide containing 5% (v/v) water, and the DP polarogram was recorded. The PMASDA content was determined based on a calibration graph plotted by means of solutions obtained by adding 20, 40, 60, 80, or 100 μl of a methanolic solution of pure PMASDA to the polarographic vessel, evaporating the solvent, and dissolving the residue in the above supporting electrolyte.

RESULTS AND DISCUSSION

Checking the Purity of the PMASDA Preparation and Stability of Its Stock Solutions

The PMASDA content of the recrystallized chemical used to prepare the stock solutions was checked by procedures as described in the Experimental. Oxidimetric and precipitation titrations revealed 99.0% and 99.1% contents, respectively. Thin layer chromatography gave evidence that the chemical consisted of a single compound. The UV spectrum of the PMASDA solution in dimethylformamide, c = 20 μmol l^{-1}, is shown in Fig. 1. Spectrophotometric determination of substances of this kind is generally aggravated by their *cis–trans* isomerism[1]. The *trans* form converts to the *cis* form under the effect of light. The latter form does not fluoresce due to the loss of coplanarity[18], and the absorption spectrum exhibits a hypsochromic shift and absorptivity decrease. Therefore, the absorption spectra of such substances are usually measured immediately after solution preparation in darkness, or else their absorbances are measured in the isosbestic point, where they are unaffected by the *cis–trans* isomerism. The PMASDA solution in dimethylformamide exhibited absorption maxima at 270 and 360 nm and the isosbestic point at 328 nm. The molar absorptivities at 360 nm and in the isosbestic point, viz. 5.41 . 10^4 and 2.84 . 10^4 l mol^{-1} cm^{-1}, respectively, are consistent with published data[1,18]. The stability of the PMASDA stock solutions in dimethylformamide (c = 1 mmol l^{-1}) was also examined by DPP at a DME: no changes beyond the experimental error were observed within a period of 30 days from the solution preparation.

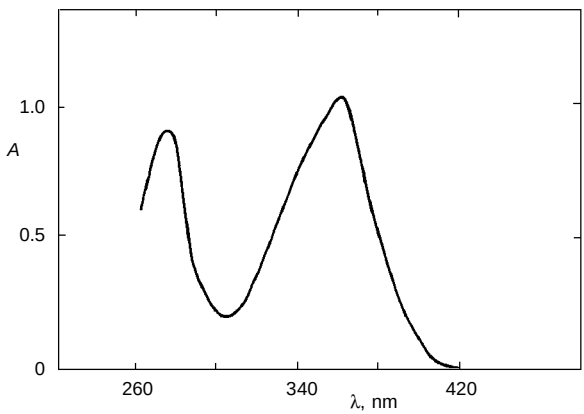


FIG. 1
UV absorption spectrum of PMASDA solution in dimethylformamide, c = 20 μmol l^{-1}. Optical pathlength 1 cm

Tast Polarography and Differential Pulse Polarography Using a Conventional Dropping Mercury Electrode

Preliminary experiments revealed that aqueous and aqueous–alcoholic (1 : 1) solutions containing the Britton–Robinson buffer at pH 2–12 or 0.1 M NaOH or 0.1 M H_2SO_4 are unsuitable for the polarographic determination of PMASDA. No wave or peak could be observed either, when using methanol, dioxane, or acetonitrile, containing 5–25% water in the presence of 0.1 mol l^{-1} tetraethylammonium bromide as the supporting electrolyte. Nonaqueous dimethylformamide is also unsuitable because of frequent record failures due to irregularities in the mercury dropping patterns.

Dimethylformamide containing 5% (v/v) water and tetraethylammonium bromide were finally chosen as a system allowing waves and/or peaks to be recorded as far as –2.7 V vs SCE. This medium has been employed with success during the polarographic determination of the structurally related 4,4′-bis[(4-phenylamino-6-methoxy-1,3,5-triazin-2-yl)amino]stilbene-2,2′-disulfonic acid. In such medium, PMASDA at a concentration of 300 μmol l^{-1} exhibits two waves/peaks in tast/DP polarography (Fig. 2). The first wave at $E_{1/2}$ = –2.02 V or peak at E_p = –1.99 V apparently corresponds to the reduction of sodium ions. The DC polarographic wave height is directly proportional to the square root of mercury reservoir height and to the sodium ion concentration, as demonstrated by addition of NaCl. The other wave at $E_{1/2}$ = –2.31 V or peak at E_p = –2.29 V is apparently due to the reduction of the stilbene double bond.

The wave and peak due to the sodium ion reduction are analytically unusable because practical samples always contain some amounts of inorganic ions affecting the

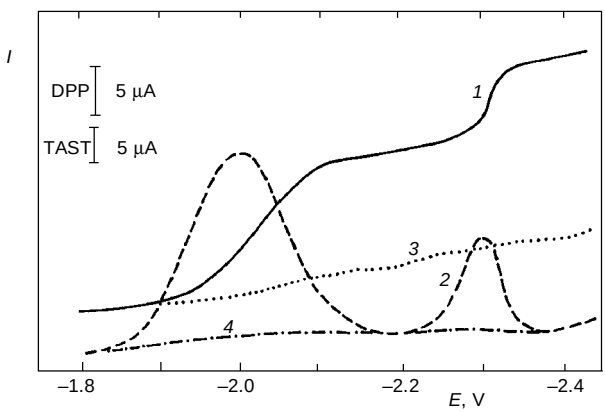


FIG. 2
Tast (*1*, *3*) and DP (*2*, *4*) polarograms of PMASDA solution (c = 300 μmol l^{-1}) in dimethylformamide containing 5% (v/v) water and 0.01 mol l^{-1} tetraethylammonium bromide (*1*, *2*) and of the supporting electrolyte alone (*3*, *4*)

wave and peak height. Therefore, attention was focussed on the wave due to the reduction of the C=C double bond.

The solutions polarographed were found sufficiently stable: the DPP peak decrease in 1 h from the solution preparation was no higher than 1% at a PMASDA concentration of 300 μmol l^{-1}, and 4% at a PMASDA concentration of 30 μmol l^{-1}. No E_p shift due to *cis-trans* isomerization was observed within 60 min. The $I_{lim}/(m^{2/3}\ t^{1/6})$ value where I_{lim} is the limiting current of the second wave as obtained by tast polarography, m is the mercury mass flow rate, and t is the electronically controlled drop time, was constant over the drop time range of 1–4 s and mercury reservoir height range of 25–64 cm. Hence, it is reasonable to conclude that the limiting current is due to a diffusion-controlled phenomenon. The shape of the second wave and its semilogarithmic analysis indicate an irreversible nature of the phenomenon. The above conclusions are borne out by the dependences of the second DPP peak potential and height on the pulse magnitude and polarization rate. The irreversible nature of the process is also corroborated by the absence of an anodic peak in the cyclic voltammetric record using an HMDE at polarization rates of 50–500 mV s^{-1}. Because of the different diffusion coefficients of sodium ions and the analyte dianion, the height ratio of the corresponding waves does not allow conclusions to be drawn concerning the number of electrons exchanged during the C=C double bond reduction. Hence, it is impossible to decide unambiguously whether the second wave is due to a two-electron reduction of PMASDA or to a single-electron reduction followed by accepting a proton. In the latter case the wave corresponding to the exchange of the second electron would be overlapped by the supporting electrolyte decomposition. In a dimethylformamide solution containing 5% (v/v) water and 0.01 mol l^{-1} tetrabutylammonium iodide, unsubstituted *trans*-stilbene provides two waves at –2.18 and –2.56 V vs SCE (ref.[19]). Therefore we consider it more likely that the wave observed for the analyte under study corresponds to the single-electron reduction of PMASDA to the radical-anion *II*, which is stabilized immediately by accepting a proton as shown in Scheme 1. The subsequent reduction of the free radical *III* so formed is apparently overlapped by the current due to the decomposition of the supporting electrolyte.

A comparison of the half-wave potentials of PMASDA and 4,4′-bis[(4-phenylamino-6-methoxy-1,3,5-triazin-2-yl)amino]stilbene-2,2′-disulfonic acid[4] demonstrates that the polarographic method does not allow the two substances to be discriminated and that the substituents at the triazine system have virtually no effect on the position of the wave due to the reduction of the stilbene double bond.

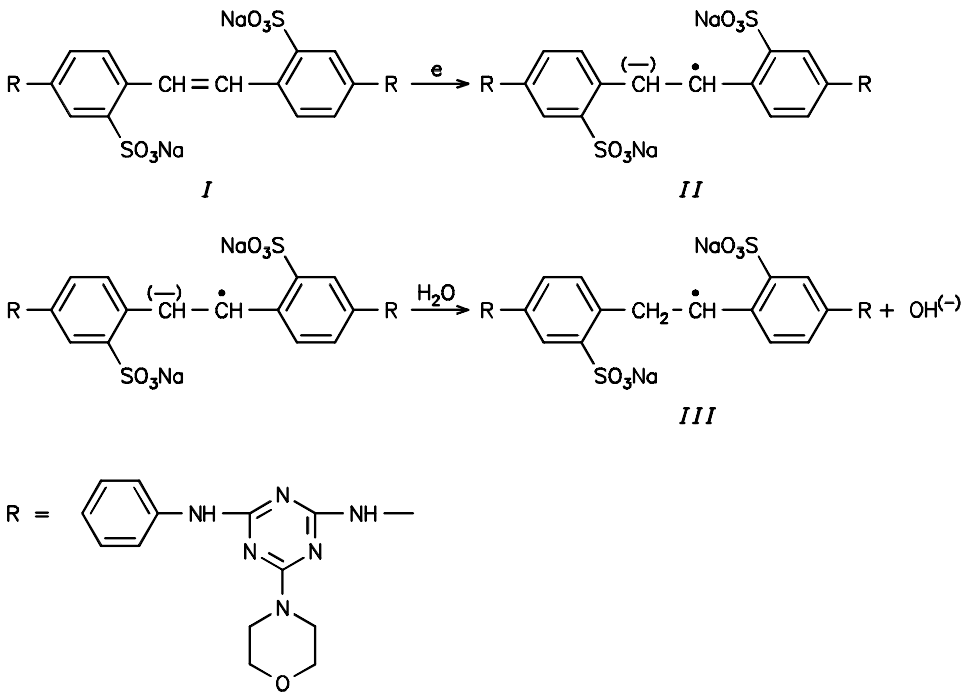
The dependences of the wave and peak heights on the PMASDA concentration in a 0.01 M tetraethylammonium bromide solution in dimethylformamide containing 5% (v/v) water are linear over the concentration ranges of 100–500 μmol l^{-1} for tast polarography and 10–500 μmol l^{-1} for DP polarography (Table I). Lower concentrations cannot be quantitated because of the highly negative half-wave or peak potential. De-

crease in the tetraethylammonium bromide concentration brings about a smoother supporting electrolyte baseline, lowering the limit of determination.

Furthermore, it was confirmed that for the pure substance free from inorganic impurities, its concentration can be determined based on the height of the peak due to the sodium ion reduction, by means of a calibration straight line plotted by using sodium chloride. However, this approach would be inapplicable in practice where impurities containing sodium ions are frequently present.

Differential Pulse Voltammetry Using a Hanging Mercury Drop Electrode

The parameters of the concentration dependences measured in the DPP mode are given in Table I and the voltammograms are shown in Fig. 3, which also displays the method of evaluation. At concentrations of 300 μmol l^{-1} and higher, the peaks due to the reduction of the double bond and the reduction of sodium ions overlap partly. To preserve linearity, the peak height must then be determined by some alternative procedure, such as measuring the distance between the straight lines which pass through the peak maximum and the more negative minimum and are parallel to the axis of abscissas.



SCHEME 1

TABLE I

Calibration curve parameters for the polarographic and voltammetric determination of PMASDA in dimethylformamide containing 5% (v/v) water and 0.01 mol l^{-1} tetraethylammonium bromide; *r* is the correlation coefficient, L_Q is the limit of determination

Method	*c*, mol l^{-1}	Slope mA mol^{-1} l	Intercept μA	*r*	L_Q μmol l^{-1}
TAST/DME	(1– 5) . 10^{-4}	26.9	0.18	0.9997	40
DPP/DME	(1– 5) . 10^{-4}	35.1	–0.12	0.9997	–
DPP/DME	(1–10) . 10^{-5}	33.5	–0.05	0.9985	17
DPP/DME	(1–10) . 10^{-5a}	19.9	–0.04	0.9991	5
DPV/HMDE	(1– 5) . 10^{-4}	26.4	0.3	0.9975	–
	(1–10) . 10^{-5}	30.6	0.11	0.9985	–
	(1–10) . 10^{-5a}	13.9	–0.01	0.9992	–
	(1–10) . 10^{-6a}	18.0	0.001	0.9988	1.8
LSV/HMDE	(1– 5) . 10^{-4}	24.8	1.2	0.9799	–
	(1–10) . 10^{-5}	34.9	–0.05	0.9901	–
	(1–10) . 10^{-5a}	14.0	–0.05	0.9969	4.1

[a] Tetraethylammonium bromide concentration 0.001 mol l^{-1}.

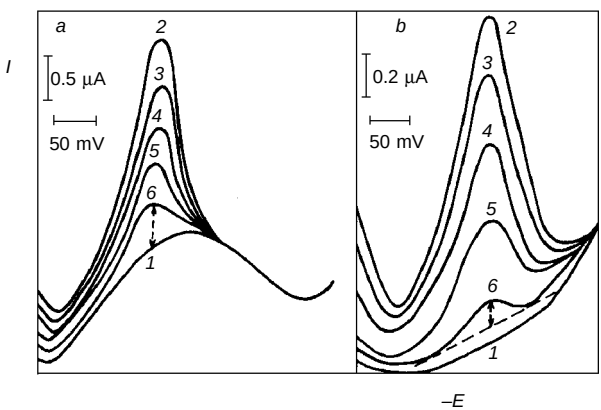


FIG. 3

DP voltammograms at an HMDE for PMASDA solutions in dimethylformamide containing 5% (v/v) water and 0.01 mol l^{-1} (*a*) or 0.001 mol l^{-1} (*b*) tetraethylammonium bromide. PMASDA concentration (μmol l^{-1}): *1* 0, *2* 100, *3* 80, *4* 60, *5* 40, *6* 20. Starting potential: –2.15 V (*a*) and –2.25 V (*b*). Dashed line is the baseline from which the peak height was read

The correlation coefficients and DP voltammogram shapes suggest that when quantitating PMASDA concentrations lower than 100 μmol l^{-1} it is convenient to use a 10-fold more dilute tetraethylammonium bromide solution, although the slope of the concentration dependences is then somewhat lower. This lowering may be due to a change in the composition of the electrode double layer and its effect on the electrode reaction rate.

Furthermore, it was found that the surface of the HMDE, which does not renew during the measurement, undergoes passivation. This brings about, among other things, a considerable decrease in the height of the peak obtained in the DPP mode at the SMDE if the drop time is extended or if the recording is performed from more negative towards more positive potentials. At a polarization rate of 5 mV s^{-1} the height of the peak corresponding to the double bond reduction is one-half as compared to that obtained at a polarization rate of 2 mV s^{-1}. This may be associated with the adsorptive accumulation of analyte on the SMDE surface. DP voltammograms of PMASDA within the lowest attainable concentration range are shown in Fig. 4.

Adsorptive Stripping Voltammetry Using a Hanging Mercury Drop Electrode

The DPV peak of PMASDA increases with time elapsed between the drop formation and voltammogram recording. This effect, which is apparently associated with the adsorptive accumulation of analyte on the HMDE surface, is most marked at accumulation potentials more negative than –2.00 V, i.e. behind the maximum of the sodium ion reduction peak. This suggests that the adsorption process is affected by reduction of sodium ions.

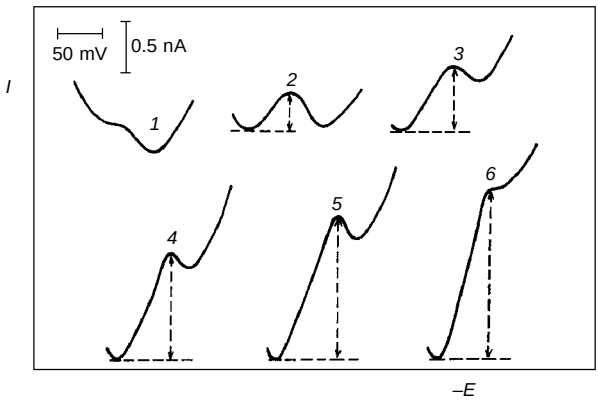


FIG. 4

DP voltammograms at an HMDE for PMASDA solutions in dimethylformamide containing 5% (v/v) water and 0.001 mol l^{-1} tetraethylammonium bromide. PMASDA concentration (μmol l^{-1}): *1* 1, *2* 2, *3* 4, *4* 6, *5* 8, *6* 10. Starting potential –2.25 V. Dashed lines indicate how the peak height was read

The concentration dependences could not be measured at concentrations lower than 1 μmol l^{-1} because of the unfavourable shape of the supporting electrolyte line at highly negative potentials. No improvement could be achieved by extending the time of accumulation, reducing the supporting electrolyte concentration, or additionally purifying the dimethylformamide and tetraethylammonium bromide chemicals.

Linear Sweep Voltammetry Using a Hanging Mercury Drop Electrode

The applicability of LSV using an HMDE was examined with a view to increasing the sensitivity of PMASDA determination. Table I documents, however, that the limit of determination by LSV is twice as high as in the DPV mode.

Practical Application of the Methods Developed

Practical applicability of the new methods of determination was tested on the technical agents Blankophor MBBH and Rylux D as described in Experimental. The values obtained (Table II) are in a very good agreement with those obtained by oxidimetric titration. Moore's u-test gave evidence that the results of the polarographic and oxidimetric analyses are identical at the 95% confidence level. The slightly higher results found by precipitation titration with a cation-active substance can be explained by the presence of an anion-active tenside added to the commercial agents. For the samples studied, the presence of this tenside did not bring about distortion of the polarographic curves. Still, for more complex practical samples it is better to apply the method of two standard additions or to separate PMASDA from the sample by TLC (see Experimental) prior to analysis.

TABLE II

Results of determination of PMASDA in technical samples by various analytical methods; the values are averages of 3 determinations, from which the relative standard deviation estimate was also calculated

Sample	Concentration, %/Relative standard deviation, %			
	$KMnO_4$[a]	Septonex[b]	TAST[c]	DPP[d]
Pure substance[e]	99.0/0.3	99.1/0.3	–	–
Blankophor MBBH[f]	51.1/0.5	53.9/0.6	51.5/1.8	52.1/2.2
Rylux D[f]	54.9/0.3	56.0/0.4	55.4/2.0	55.8/2.1

[a] Oxidimetric titration with potassium permanganate; [b] precipitation titration with Septonex; [c] tast polarography; [d] differential pulse polarography; [e] sample employed to obtain calibration plots for tast and DPP analysis; [f] commercial products.

The procedure described in Experimental was applied to the determination of PMASDA by DPV using an HMDE, performed after thin layer chromatographic separation of the analyte. The recovery from the entire procedure was first examined using the pure chemical. The results are given in Table III; the data were read from a calibration plot constructed by adding 10, 20, 40, 60, 80, or 100 μl of a $1 . 10^{-3}$ mol l^{-1} methanolic solution of pure PMASDA to the polarographic vessel, evaporating the solvent, and diluting the residue in the supporting electrolyte solution. Table III demonstrates that except for the first case, the standard deviation did not exceed 4% and the recovery was between 95% and 99%. The stock solution of PMASDA in dimethylformamide can also be used but the process takes a longer time due to the necessity of drying the chromatogram with warm air for 20 min after applying the dimethylformamide solution.

TABLE III
Recovery from the process of PMASDA determination by DPV at an HMDE following separation by TLC; the values are averages of 5 determination, *s* is the standard deviation

Added, μg	43.1	86.1	172.2	258.3	344.4	430.5
Found, μg	40.9	82.6	166.9	251.6	341.0	422.5
Found, %	94.9	95.8	96.9	97.4	99.0	98.1
s, %	7.1	3.5	3.4	3.0	1.9	1.8

TABLE IV
Determination of PMASDA in technical products by DPV at an HMDE following separation by TLC; the values are averages of 5 determinations

	Sample	
	Blankophor MBBH	Rylux D
Technical product added, μg	86.1	96.1
PMASDA content, %	51.1[a]	54.9[a]
PMASDA found, μg	41.7	51.3
PMASDA found, %	48.4	56.2
Relative standard deviation, %	5.8[b]	4.6[b]

[a] Found by oxidimetric titration; [b] for the determination by DPV at an HMDE following separation by TLC.

Thin layer chromatography with a suitable eluent can be employed for rapid separation of PMASDA from other optical whitening agents or impurities. The method developed, including the subsequent voltammetric determination, can be applied to the quantitation of PMASDA in commercial products, as tested on Blankophor MBBH and Rylux D. The procedure was the same as for the pure chemical, modified so that 20 μl of a methanolic solution of the commercial product was applied to the start of the thin layer. The results agree well with those obtained by oxidimetric titration (Table IV). The data were read from a calibration plot constructed by using the pure analyte. The standard addition method, which is less time consuming, can also be used with advantage if few samples are to be analyzed.

CONCLUSIONS

The new methods for the polarographic or voltammetric determination of PMASDA can be applied in the technological manufacturing process and technical product control as well as in the environmental monitoring of wastewaters. This is valuable in view of the potential mutagenic effects of some derivatives of 4,4′-diaminostilbenedisulfonic acid. Prior to the analysis of a complex matrix, however, the analyte should be separated by a suitable method such as thin layer chromatography.

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