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

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Received June 16, 1993
Accepted October 5, 1993

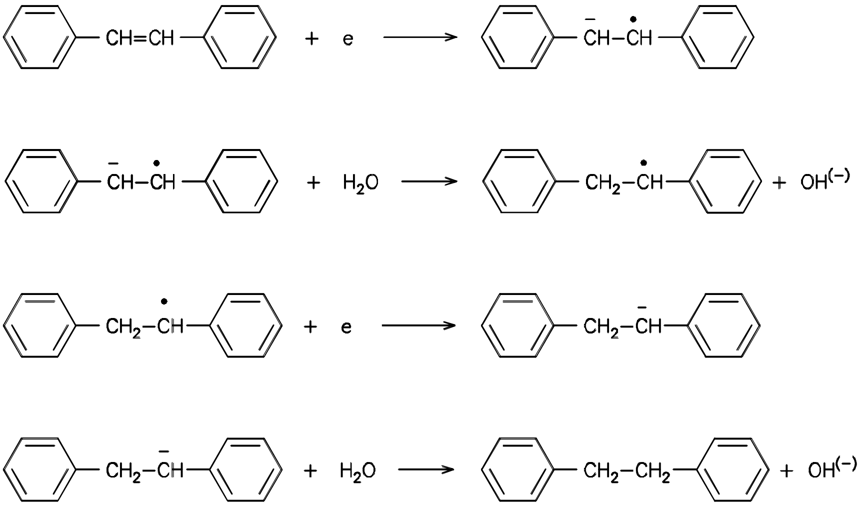
The polarographic and voltammetric behaviour was examined for the title compound, which is the basic component in many commercial optical whitening agents. Dimethylformamide containing 5 vol.% water was chosen as the solvent and tetraethylammonium bromide as the supporting electrolyte. The optimum conditions were found for determining the substance by tast polarography, differential pulse polarography, linear sweep voltammetry on a hanging mercury drop electrode, and differential pulse voltammetry on a hanging mercury drop electrode. The analyte concentration regions for the four techniques were 0.1 – 0.5, 0.01 – 0.5, 0.01 – 0.5 and 0.01 – 0.1 mmol l^{-1}, respectively. Practical applicability of the methods to the determination of the title compound in technical products was verified.

4,4′-Bis[(4-phenylamino-6-methoxy-1,3,5-triazin-2-yl)amino]stilbene-2,2′-disulfonic acid (BASDA) is the basic component of many commercial optical whitening agents such as Uvitex CF (Ciba–Geigy, Basel, Switzerland) and Rylux PRS Supra (VCHZ Synthesia, Pardubice, The Czech Republic). This substance can be determined by oxidimetric titration with potassium permanganate[1], by precipitation titration with cetylpyridinium chloride[2], tetrabutylammonium chloride or iodide[3], methylene blue[4], or [1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide[5]. UV spectrophotometry[6 – 9] and fluorometry[6,8,10 – 13] can be employed as well. Preliminary separation can be achieved by using extraction[14], paper chromatography[14] or thin layer chromatography[6,14]. There are two functional groups in a molecule of BASDA which can play a role in its polarographic behaviour, viz. the triazine ring and the C=C bond of the stilbene system.

Some 4,4′-bis(triazinylamino)stilbene-2,2′-disulfonic acid derivatives have been studied by AC polarography and AC oscillopolarography[15–19]. The sulfo group was found to play a major role in the adsorption process, whereas the substituent at the triazine ring has no effect on the peak potential[15]. A measurable desorption peak has been observed[16] at –1.1 V vs SCE for the *trans*-derivative and at more positive values for the *cis*-derivative[19].

Several papers have dealt with the reduction of 1,3,5-triazines[20 – 23], mostly in rather complex substances serving as herbicides. Some substituted 1,3,5-triazines provide well-developed waves whereas others are inactive across the entire pH region. Adsorption stripping voltammetry[24,25], oxidation at a rotating disk platinum electrode in acetonitrile medium[26] and, for chlorine substituted derivatives, formation of insoluble mercury salts[27] have also been employed.

The polarographic reduction of the C=C double bond in stilbene and its derivatives has received attention[28 – 38]. The investigation was mostly performed in dioxane, dimethylformamide or acetonitrile containing 0 to 25% water and in the presence of tetrabutylammonium iodide or tetraethylammonium bromide. Tetrahydrofuran[29] and butanol[30] or ethanol[31] in mixtures with water have also been used occasionally. Various stilbene derivatives provide, in dependence on medium, waves with $E_{1/2}$ within the range of −2.1 to −2.8 V vs SCE. Highly negative potentials are rather inconvenient from the polarographic point of view, particularly if the substances are to be quantitated in complex matrices. The mechanism of reduction of the C=C bond in stilbene derivatives has been studied in detail in ref.[32]. Stilbene gives two waves in nonaqueous media such as acetonitrile and dimethylformamide. The second wave decreases as the water content of the solvent is increased, while the first wave increases to reach a limit in which its height equals the sum of heights of the two waves in the nonaqueous medium. The difference between the heights of the two waves is determined, as well as by the water content, by the acid-base properties of the solvent. The following ECEC mechanism of two-electron reduction of stilbene in the presence of water (a single wave) has been suggested (Scheme 1).



SCHEME 1

This mechanism has been confirmed by refs[33,34]. The reduction of stilbene on a disk platinum electrode in tetrahydrofuran and tetrabutylammonium perchlorate solutions also proceeds in two one-electron steps[29]. The effect of alkyl substituents on the $E_{1/2}$ value of reduction of stilbene derivatives has been the concern of ref.[35]. The environment of the double bond has been observed to little affect the $E_{1/2}$ value[36].

No mention of the polarographic behaviour of BASDA was found in the literature. The behaviour of that substance in tast polarography and differential pulse polarography (DPP) on a conventional dropping mercury electrode (DME) and in linear sweep voltammetry (LSV) and differential pulse voltammetry (DPV) on a hanging mercury drop electrode (HMDE) is the subject of this paper. Dimethylformamide containing 5 vol.% water served as the solvent, and tetraethylammonium bromide was used as the supporting electrolyte. With this medium it was possible to apply highly negative potentials required to reduce the double bond of the stilbene system in the BASDA molecule.

EXPERIMENTAL

Reagents

Disodium BASDA ($C_{34}H_{28}N_{10}S_2O_8Na_2$, CAS name: 2,2′-(1,2-ethenediyl)bis{5-[(4-methoxy-6-phenylamino)-1,3,5-triazin-2-yl]amino}benzenesulfonic acid, disodium salt, CAS Registry Number 3426-43-5, Ciba–Geigy, Basel, Switzerland) was obtained by double recrystallization of the technical product Uvitex CF from a water–methanol 1 : 1 mixture. The stock solution of the substance (c = 1 mmol l^{-1}) in dimethylformamide was prepared by dissolving 0.8148 g in the solvent and diluting to 1 000 ml. More dilute solutions were obtained by precise dilution of the stock solutions with dimethylformamide. The purity and active content in the preparations used were checked by oxidimetric and precipitation titrations, thin layer chromatography, and spectrophotometry (see later). To prevent *cis–trans* isomerization, the solutions were prepared, diluted and stored in dark, and measurements were conducted in brown glass vessels.

Dimethylformamide pure (Lachema, Brno, The Czech Republic) was multiply vacuum redistilled with potassium hydroxide[39] prior to use. Tetraethylammonium bromide pure (Lachema, Brno, The Czech Republic) was recrystallized from a water–methanol 1 : 1 mixture. Septonex ([1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide) in a purity conforming to PhBS 4 (Slovakofarma, Hlohovec, The Slovak Republic) and sodium lauryl sulfate of reagent grade purity (Lachema, Brno, The Czech Republic) were used in the titrations.

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

Apparatus

A PA 4 polarographic analyzer interfaced to an XY 4105 plotter (both Laboratorni pristroje, Prague, The Czech Republic) was used, applying the three-electrode connection involving an auxiliary platinum sheet electrode. A saturated silver chloride electrode served as the reference electrode, connected to the analytical solution through a salt bridge containing tetraethylammonium bromide (0.1 mol l^{-1}) in dimethylformamide. To comply with the conventional presentation, the potentials were converted vs SCE. A conventional DME (in tast polarography and DPP) and an SMDE 1 static mercury drop electrode (Laboratorni pristroje, Prague, The Czech Republic) in the HMDE mode served as the working electrodes.

The DME reservoir height was 25 cm. The drop time in 0.1 M potassium chloride at 0 V was 8.91 s, the mass flow rate was 0.38 mg s^{-1}. The HMDE capillary was 0.138 mm in diameter and the largest drop possible was used (valve open for 160 ms).

The following parameters were applied unless stated otherwise: potential sweep rate 5 mV s^{-1} in tast polarography and DPP and 20 mV s^{-1} in LSV and DPV, electronically controlled drop time of 1 s, and pulse height of −50 and −25 mV in DPP and DPV, respectively.

Oxygen was removed from the solutions by nitrogen purging. For this, nitrogen was purified by passing through a solution of chromium(II) ions in dilute (1 : 1) hydrochloric acid over zinc amalgam. A bubbler containing the same supporting electrolyte as the measuring cell was inserted before that cell.

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

Oxidimetric potentiometric titrations were performed with an OP 208/1 pH-meter (Radelkis, Hungary) equipped with a platinum wire indicator electrode and a saturated calomel reference electrode. An MM 6 electromagnetic stirrer (PM, Poland) was also employed. Precipitation titrations were carried out on a Spekol 11 spectrocolorimeter equipped with a Ti titration adapter (Zeiss, Jena, Germany) with a built-in electromagnetic stirrer. The wavelength was 700 nm, cell volume 30 ml.

Thin layer chromatography was conducted with a commercial kit on Silufol UV 254 plates (Kavalier, Votice, The Czech Republic). An M 415 centrifuge (Chirana, The Czech Republic) and a Unipan 350 rotary vacuum evaporator (Poland) were employed during the purification and separation processes.

All measurements were made at room temperature.

Procedures

Polarographic and voltammetric measurements. A volume of 1.00 ml of tetraethylammonium bromide solution (c = 0.1 mol l^{-1}) in dimethylformamide in a 10 ml volumetric flask was mixed with 0.5 ml of redistilled water and the requisite volume of BASDA solution in dimethylformamide, and diluted to volume with dimethylformamide. Nitrogen purging was applied for 10 min and the polarographic or voltammetric curve was recorded.

Calibration curves were measured in triplicate and subjected to linear regression using the least squares method. The limit of determination L_Q was calculated as tenfold the standard deviation of 7 determinations of analyte at a concentration corresponding to the lowest point of the calibration curve[40].

Oxidimetric titration. The method based on the oxidation of the stilbene double bond[1] giving two molecules of the corresponding aldehyde was employed. The procedure was as follows. An amount of 0.1000 g of sample was dissolved in 50 ml of redistilled water, and 0.5 g of each of sodium chloride and sodium hydrogencarbonate were added. The mixture was titrated with potassium permanganate (c = 0.033 mol l^{-1}) with potentiometric control using a platinum indicator electrode and a saturated calomel reference electrode. Since the potential established slowly, the titration curve points were read 2 min after adding the titrant. The measurements were made at the room temperature. One ml of the potassium permanganate solution, c = 0.033 mol l^{-1}, corresponded to 0.0204 g BASDA. The potassium permanganate titre was determined by titration of oxalic acid in sulfuric acid solution[41].

Precipitation titration. Septonex served as the titrant for BASDA in precipitation titrations. One molecule of analyte reacts with 2 molecules of titrant[5].

Procedure: an amount of 0.075 g of sample was dissolved in a water–ethanol 2 : 1 mixture in a 500 ml volumetric flask and diluted to volume with that mixture. A 20.00 ml aliquot was titrated in a 30 ml cell with a solution of Septonex (c = 6.50 mmol l^{-1}), prepared by dissolving 2.8 g of the substance in 1 000 ml of water. The titration end point was determined turbidimetrically at 700 nm; this wavelength was chosen with regard to the own fluorescence and absorption of analyte. One ml of Septonex titrant solution (c = 6.50 mmol l^{-1}) corresponded to 2.648 mg of BASDA. Titrant was standardized by two-phase precipitation titration of sodium lauryl sulfate[5] using an acid mixture of dimidium bromide and disulfine blue (2 : 1) as the indicator.

Polarographic determination of BASDA in Uvitex CF and Rylux PRS Supra. About 0.1 g of sample was weighed precisely, dissolved in dimethylformamide in a 50 ml volumetric flask, and made up to the mark with that solvent. An aliquot of 1.00 ml was pipetted into a 10 ml volumetric flask, 1.00 ml of tetraethylammonium bromide solution (c = 0.01 mol l^{-1}) in dimethylformamide and 0.50 ml of redistilled water were added, the solution was made up to the mark with dimethylformamide, and the tast or DP polarogram was recorded after nitrogen purging. Analyte concentration was determined by using calibration plots obtained with the pure substance.

TLC purity testing. A volume of 10 μl of BASDA solution ($c \approx$ 1 mmol l^{-1}) in dimethylformamide was applied to the start and solvent was removed with warm air stream. The ascending mode was used. All work, from the solution preparation to the drying of the chromatogram developed, was conducted in a dark room using red light, elution proceeded in a covered tank. Short exposure to an UV lamp was applied for detection.

The following mobile phases were employed: methanol–ammonia–water 10 : 4 : 1 (R_F = 0.84), chloroform–methanol–ammonia 12 : 7 : 2 (R_F = 0.60), acetone–benzene–water–ammonia–0.1 M tetrabutylammonium iodide 70 : 20 : 7 : 4 : 2 (R_F = 0.55), and benzene–dioxane–methanol–ammonia 5 : 4 : 2 : 1 (R_F = 0.25). The purified chemical displayed a single spot in all cases, which gives evidence that a single compound was involved.

TLC separation of BASDA from Uvitex CF and Rylux PRS. An amount of 0.1000 g of sample was dissolved in 10.00 ml of methanol, and 50 μl of the solution were applied to the start of a TLC plate. The ascending mode was used for development in saturated vapours of a chloroform–methanol–ammonia 12 : 7 : 2 mixture. After drying the chromatogram and detecting the spot by short UV irradiation, a rectangle about 1.5 × 3.5 cm containing the spot was cut out, cut into a tip, and suspended in a dish containing a methanol–ammonia 4 : 1 elution mixture. This mixture was used to wash out the spot directly into the polarographic vessel. The solvent was evaporated in a stream of warm air, the residue was dissolved in a solution of tetraethylammonium bromide (0.001 mol l^{-1}) in dimethylformamide containing 5 vol.% water, and the DP polarogram was recorded. The calibration straight line was obtained by pipetting 20, 40, 60, 80 and 100 μl volumes of BASDA solution in methanol into the polarographic vessel, evaporating the solvent, and dissolving the residue in the supporting electrolyte as above.

RESULTS AND DISCUSSION

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

Preliminary experiments gave evidence that aqueous and aqueous-methanolic 1 : 1 solutions containing a buffer at pH 2 – 12 or 0.1 M NaOH or 0.1 M H_2SO_4 are unsuitable for polarographic determination of BASDA. No wave or peak was also observed when using methanol, dioxane or acetonitrile containing 5 – 25% water, invariably in the presence of tetraethylammonium bromide (c = 0.1 mol l^{-1}) as the supporting electrolyte.

Dimethylformamide was finally chosen as the solvent. With this solvent and using tetraethylammonium bromide as the supporting electrolyte, waves and peaks could be recorded as far as −2.7 V vs SCE. Also, dimethylformamide has been used during the polarographic study of stilbene derivatives[32 – 34].

In this medium, the analyte at c = 0.3 mmol l^{-1} provides two waves/peaks in tast/DP polarography. The first wave, at $E_{1/2}$ = –2.01 V, clearly corresponds to the reduction of sodium ions. An irreversible, diffusion-controlled phenomenon is involved: the DC polarographic wave is directly proportional to the mercury reservoir height root and to the sodium ion concentration. The second wave, $E_{1/2}$ = −2.27 V, or peak, E_p = −2.25 V, apparently corresponds to the reduction of the stilbene double bond.

The former wave or peak, corresponding to sodium ion reduction, is analytically unusable because practical samples always contain some inorganic salts which affect the height of that wave/peak. Major attention was therefore paid to the wave due to the reduction of the C=C double bond. Nonaqueous dimethylformamide appeared unsuitable for the quantitation due to frequent distortions of the record associated with irregular dropping of mercury. This drawback was eliminated by adding some quantity of water. The effect of water content on the DP polarograms of BASDA is shown in Fig. 1, demonstrating that as the water content is increased, the peak corresponding to the double bond reduction shifts to more positive potentials to finally merge with the peak belonging to the sodium ion reduction. A concentration of 5 vol.% water emerged as optimum and was used in the subsequent measurements unless stated otherwise. In such medium containing tetraethylammonium bromide (0.01 mol l^{-1}) as the supporting electrolyte, the analyte gives both well-developed DPP peaks and well-developed tast polarographic waves which are easy to evaluate (Fig. 2).

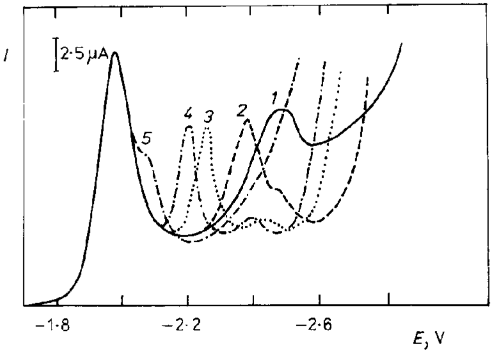


FIG. 1
Effect of water content in dimethylformamide on DP polarograms of BASDA (c = 0.3 mmol l^{-1}) on a DME in the presence of 0.01 M tetraethylammonium bromide. Water content (vol.%): *1* 0, *2* 1, *3* 5, *4* 10, *5* 25

The solutions polarographed are sufficiently stable: for solutions containing BASDA in concentrations of 0.3 and 0.03 mmol l^{-1}, the DPP peaks decreased no more than 1% and 4%, respectively, in 1 h from the solution preparation. No E_p shift indicating *cis–trans* isomerization was observed within a time of 60 min. The value of $k = I_{lim}/(m^{2/3}\ t^{1/6})$ where I_{lim} is the limiting tast polarographic current corresponding to the second wave, m is the mercury mass flow rate, and t is the electronically controlled drop time, was constant within the drop time span of 1 – 4 s and the mercury reservoir height span of 25 – 64 cm. Hence, the limiting current can be regarded as diffusion-controlled. The shape of the second wave and its semilogarithmic analysis indicate an irreversible nature of the phenomenon involved. The fact that the phenomenon is irreversible and diffusion-controlled is also borne out by the dependence of the position and height of the second DPP peak on the pulse amplitude and polarization rate. No conclusions concerning the number of electrons exchanged during the double bond reduction can be drawn from the observed height ratio of the wave due to the sodium ion reduction to the wave due to the double bond reduction, because the sodium ions and the dianion of the substance possess different diffusion coefficient values. Therefore, one cannot determine unambiguously whether the wave corresponds to the two-electron reduction of BASDA according to Scheme 1 or to a one-electron reduction only, with subsequent acceptance of a proton according to the first half of the scheme. In the latter case the wave corresponding to the exchange of the second electron would be overlapped by the supporting electrolyte decomposition wave. This concept is supported by the fact reported in ref.[33], viz. that unsubstituted *trans*-stilbene gives two waves, at –2.18 and –2.56 V vs SCE, in dimethylformamide containing 5 vol.% water and 0.01 mol l^{-1} tetrabutylammonium iodide. In addition to tetraethylammonium bromide, other supporting electrolytes were tested, viz. tetrabutylammonium iodide, tetramethylammonium bromide, and tetramethylammonium chloride, which, however, did not appear so well suited with respect to the shape of the baseline.

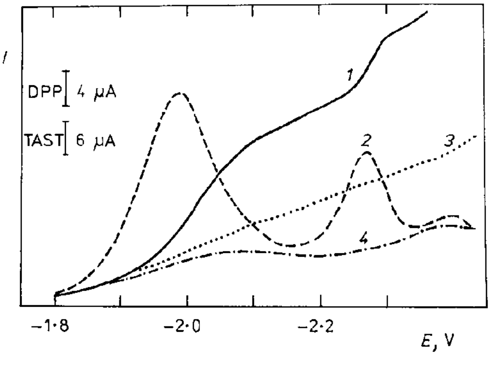


Fig. 2

Tast (*1*, *3*) and DP (*2*, *4*) polarograms of BASDA (c = 0.3 mmol l^{-1}) (*1*, *2*) and blank solution (*3*, *4*). Medium of dimethylformamide containing 5 vol.% water and 0.01 M tetraethylammonium bromide as supporting electrolyte

The dependences of the wave/peak heights on BASDA concentration in dimethylformamide containing 5 vol.% water and in the presence of 0.01 M tetraethylammonium bromide were linear within the regions of 0.5 – 0.1 mmol l^{-1} in tast polarography and 0.5 – 0.01 mmol l^{-1} in DP polarography (Table I). Lower concentrations cannot be determined due to the highly negative half-wave or peak potential. Decrease in the tetraethylammonium bromide concentration brings about a smoother shape of the supporting electrolyte line and hence, lower limit of determination (Fig. 3).

If pure analyte free from inorganic impurities is used, it can be quantitated based on the height of the peak corresponding to the reduction of sodium ions, using a calibration straight line constructed with sodium chloride. However, this approach is not promising because impurities containing sodium ions will mostly be present.

Differential Pulse Voltammetry on a Hanging Mercury Drop Electrode

The concentration dependence parameters for this technique are given in Table I. The peaks corresponding to the double bond reduction and sodium ion reduction overlap partly unless the analyte concentration is lower than 0.3 mmol l^{-1}. To preserve the linearity of the dependence, the peak height must be evaluated in a different way, best by determining the distance between the straight lines parallel to the potential axis and passing through the peak top and through its more negative minimum.

Comparison of the correlation coefficients and shapes of the DP voltammograms indicates that if the BASDA concentration is lower than 0.1 mmol l^{-1}, it is convenient to use tetraethylammonium bromide in a 10-fold lower concentration although the slope of the concentration dependence will decrease slightly (this decrease is apparently associated with the possible change in the composition of the electrode double layer and its effect on the electrode reaction rate). Also, the HMDE whose surface is not renewed during the measurement exhibits passivation. This is manifested by an

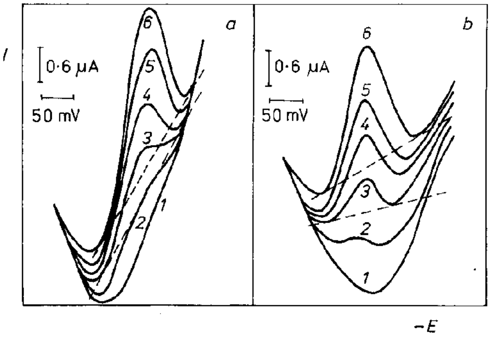


FIG. 3
DP polarograms of BASDA on a DME in dimethylformamide containing 5 vol.% water and tetraethylammonium bromide as supporting electrolyte. Tetraethylammonium bromide concentration 0.01 mol l^{-1} (*a*) and 0.001 mol l^{-1} (*b*), starting potential −2.10 V (*a*) and −2.25 (*b*). BASDA concentration (mmol l^{-1}): *1* 0, *2* 0.02, *3* 0.04, *4* 0.06, *5* 0.08, *6* 0.1. Broken line is the baseline from which the peak height was read

appreciable decrease in the DPP peak height obtained on the SMDE if the drop time is prolonged markedly or if the trace is recorded from more negative towards more positive potentials. Using the SMDE, the height of the peak corresponding to the double bond reduction is as much as twice as high for a polarization rate of 2 mV s^{-1} than for a polarization rate of 5 mV s^{-1}. This fact may be related to adsorptive accumulation of the substances on the SMDE surface.

Adsorptive Stripping Voltammetry on a Hanging Mercury Drop Electrode

The analyte peak height was found to increase with increasing time elapsed from the drop formation to the DP voltammogram recording. For unstirred medium containing BASDA in a concentration of 2 μmol l^{-1} and the supporting electrolyte in a concentration of 0.001 mol l^{-1}, and for an accumulation potential of –2.0 V, the peak heights using 0, 30, 60, 120 and 240 s of accumulation were 13, 24, 26, 28 and 20 μA, respectively. We attempted to make use of this phenomenon, which is apparently due to accumulation of the substance on the HMDE surface, to increase the sensitivity of determination. For the system as above and a time of accumulation of 60 s, the DPV peak measured at an HMDE was affected by the potential of accumulation as follows:

TABLE I
Parameters of calibration straight lines for the polarographic and voltammetric determination of BASDA in dimethylformamide containing 5 vol.% water and 0.01 mol l^{-1} tetraethylammonium bromide

Technique	Concentration, mol l^{-1}	Slope mA l mol^{-1}	Intercept μA	r^a	L_Q[b] μmol l^{-1}
Tast	$(1 - 5) . 10^{-4}$	26.4	0.02	0.9993	70
DPP	$(1 - 5) . 10^{-4}$	33.2	0.04	0.9997	–
DPP	$(1 - 10) . 10^{-5}$	27.4	–0.05	0.9998	10
DPP[c]	$(1 - 10) . 10^{-5}$	26.9	–0.02	0.9994	6
DPV	$(1 - 5) . 10^{-4}$	21.7	0.60	0.9943	–
DPV	$(1 - 10) . 10^{-5}$	19.7	0.15	0.9874	–
DPV[c]	$(1 - 10) . 10^{-5}$	12.0	0.02	0.9991	–
DPV[c]	$(1 - 10) . 10^{-6}$	7.4	0.00	0.9969	2
LSV	$(1 - 5) . 10^{-4}$	19.6	0.70	0.9839	–
LSV	$(1 - 10) . 10^{-5}$	20.8	0.06	0.9684	–
LSV[c]	$(1 - 10) . 10^{-5}$	13.9	0.00	0.9952	13

[a] Correlation coefficient; [b] limit of determination; [c] tetraethylammonium bromide concentration 0.001 mol l^{-1}.

for accumulation potentials of 0.00, –1.00, –1.50, –2.00, and –2.20 V the peak heights were 12, 13, 13, 26, and 43 nA, respectively. Hence, the effect of accumulation is most marked at potentials which are more negative than –2.00 V, that is, after the maximum of the peak corresponding to the reduction of sodium ions. This indicates that the adsorption process is affected by the process of sodium ion reduction.

The concentration dependences could not be measured at concentrations lower than 1 μmol l^{-1} because of an unsuitable shape of the supporting electrolyte baseline at highly negative potentials. The situation did not improve on extending the time of accumulation, reducing the supporting electrolyte concentration, or additional purification of dimethylformamide and tetraethylammonium bromide.

Linear Sweep Voltammetry on a Hanging Mercury Drop Electrode

LSV on a HMDE was examined in a hope that the determination of BASDA by this technique would be more sensitive. However, Table I demonstrates that the limit of determination is nearly one order of magnitude higher than in the DPV-HMDE technique.

Practical Applicability of Methods Developed

Practical applicability of the newly designed methods was tested by determining BASDA in the technical products Uvitex CF and Rylux PRS Supra using the procedure as described in the Experimental. The data (Table II) agree very well with those obtained by oxidimetric titration. Moore's u-test gave evidence that the results of the polarographic and oxidimetric determination did not differ at the 95% confidence level.

TABLE II
Results of determination of BASDA in technical samples by various techniques

Sample	Concentration, %/Relative standard deviation[a], %			
	OXIDE[b]	PRECIP[c]	TAST[d]	DPP[e]
Purified substance[f]	98.8/0.2	98.4/0.2	–	–
Uvitex CF[g]	44.6/0.4	54.8/0.6	46.7/1.3	46.8/1.9
Rylux PRS Supra[g]	48.4/0.3	46.3/0.5	50.02/2.1	50.7/1.6

[a] Averages of 3 determinations, from which the RSD values were also calculated; [b] oxidimetric titration with potassium permanganate; [c] precipitation titration with Septonex; [d] tast polarography; [e] differential pulse polarography; [f] used to set up the calibration straight lines for tast and DPP analysis; [g] commercial product.

The results obtained by precipitation titration with a cation-active substance were slightly higher, which can be explained in terms of the presence of an anion-active surfactant added to the commercial products. For the samples investigated, the presence of the surfactant did not bring about distortion of the polarographic curves. Nevertheless, for the rather complex mixtures it is convenient to apply the method of two standard additions or to separate BASDA from sample by the TLC treatment described in the Experimental. Work with the pure substance gave evidence that the recovery from this separation is better than 99.5%, the standard deviation being 2 – 5%.

CONCLUSIONS

The polarographic and voltammetric methods of determination of BASDA can find application in the production and quality control of technical products as well as in the monitoring of this analyte in waste waters into which it can get from households, laundries and industrial plants in the textile and paper fields. This is of particular importance in view of the potential mutagenity of some derivatives of 4,4′-diaminostilbenedisulfonic acid. If, however, complex matrices are to be analyzed, the analytical finish should be preceded by a suitable separation step such as thin layer chromatography.

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Translated by P. Adamek.