

## Voltammetric Determination of Dinitrotriethylbenzene

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**Abstract**—It was shown that dinitrotriethylbenzene can be determined by voltammetry at mercury-film and glassy-carbon electrodes. A procedure for determining dinitrotriethylbenzene at a glassy-carbon electrode in a reaction mixture was developed.

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Dinitrotriethylbenzene (DNTEB) is one of the most important dinitro compounds used in the synthesis of diamines from which aromatic isocyanates are obtained in the production of polyurethane foams [1]. Dinitrotriethylbenzene can be determined by classical polarography using the reduction wave of one of the nitro groups to hydroxylamine [2]. However, the use of large amounts of mercury makes the procedure very toxic.

A glassy-carbon electrode (GCE) was used for the voltammetric determination of some aromatic nitro compounds (nitrobenzene, 2-nitro-4,8-naphthalenedisulfonic acid) and products of their reduction (aniline, 2-hydroxylamino-4,8-naphthalenedisulfonic acid, and 2-amino-4,8-naphthalenedisulfonic acid) in a 0.1 M aqueous NaOH solution or in a 0.25 M NaClO<sub>4</sub> solution in DMF. The analytical range was between  $0.3 \times 10^{-2}$  and  $3.0 \times 10^{-2}$  M, and the relative error of determination was 3–5% [3]. The use of this procedure was limited by the solubility of the DNTEB-containing reaction mixture. The mixture of an aqueous KCl solution and propanol-2 was used as a supporting electrolyte for determining aromatic nitro compounds (*N,N*-diethyl-*p*-aminoazobenzene) at a rotating disk GCE in an argon atmosphere. The limiting current was a linear function of the *N,N*-diethyl-*p*-aminoazobenzene concentration in the range from  $0.25 \times 10^{-3}$  to  $2.00 \times 10^{-3}$  M. The relative error of determination was at most 2% [4]. The complex design of the electrode and the difficulty of sealing the vessel during the analysis are the drawbacks of this procedure.

Glassy-carbon electrodes in any version are free of the gravest drawback of mercury electrodes, namely, their toxicity; therefore, the goal of this work was to develop a procedure for the voltammetric determination of DNTEB at a GCE. However, we must note that, to obtain a reproducible analytical signal at a GCE, its surface should be previously prepared (cleaned and polished). A mercury-film electrode (MFE) incorporating trace amounts of mercury is proposed as an alternative indicator electrode.

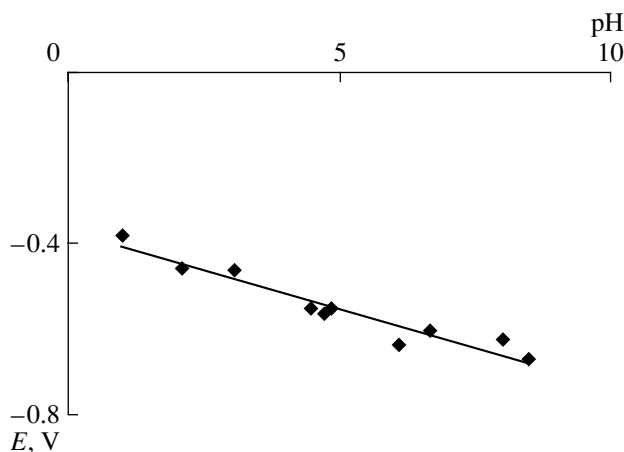
### EXPERIMENTAL

Experiments were carried out using a TA-1 voltammetric analyzer and a PU-1 universal polarograph with a two-electrode cell containing an indicator (mercury-film or glassy-carbon) electrode and a silver–silver chloride reference electrode filled with a saturated KCl solution. A 340 pH-meter was used for controlling pH. Solutions were stirred with a magnetic stirrer. An MFE was prepared by the mechanical application of metallic mercury onto a silver substrate, and a plane GCE was prepared by mirror-finishing with an Al<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>O suspension. The surface areas of the MFE and GCE were 3.0 and 12.6 mm<sup>2</sup>, respectively. Cathodic and anodic voltammograms were recorded from –0.4 to –1.4 V and from –1.4 to –0.4 V, respectively. Supporting electrolytes were prepared by mixing a 15% aqueous NH<sub>4</sub>Cl solution and ethanol, varying the ratio of components, and adjusting the required pH with 1 M HCl or 2 M NH<sub>3</sub>. A stock DNTEB solution was prepared from an accurately weighed sample (0.1000 g in 100 mL of ethanol), solutions of lower concentrations were obtained by diluting the stock solution with ethanol.

### RESULTS AND DISCUSSION

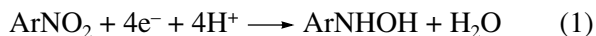
In deciding on a composition of the supporting electrolyte (NH<sub>4</sub>Cl–ethanol), we proceeded from the solubility of DNTEB and the found performance characteristics of the voltammetric determination. As the concentration of alcohol was increased, the sensitivity of determination and the solubility of the reaction mixture (methanolic–ethanolic solution of DNTEB and diamino-triethylbenzene, the semiproduct of the production of polyurethane foams) were enhanced, but the analytical range narrowed. An ethanolic solution of NH<sub>4</sub>Cl at a C<sub>2</sub>H<sub>5</sub>OH-to-NH<sub>4</sub>Cl volume ratio of 2 : 3 (pH 4.5), in which a test sample with an unknown concentration of DNTEB was well dissolved, was chosen as a supporting electrolyte.

The electroreduction of aromatic nitro compounds in acid and base solutions differ in rate, mechanism,



**Fig. 1.** Potential of the first peak of DNTEB as a function of the pH of the supporting electrolyte ( $E_{\text{acc}} = -0.4$  V;  $\tau_{\text{acc}} = 60$  s;  $v_{\text{sw}} = 7$  mV/s).

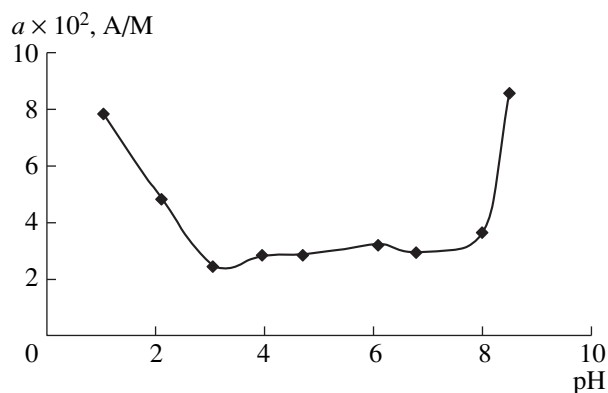
and products of reactions [2, 5]. As pH was increased, the peak potentials shifted to the region of negative potentials by 0.036 V/pH (Fig. 1). Figure 2 presents the sensitivity ( $a$ , A/M) of the voltammetric determination of DNTEB at a GCE as a function of the pH of solution. Two peaks with potentials differing by  $\sim 0.10$  V were observed in voltammograms in the pH range from 1.0 to 8.5. At pH 1.0 and 8.5, the sensitivity of determination attained a maximum. In the pH range from 3.1 to 8.0, sensitivity was virtually the same, which indicated that the composition of the supporting electrolyte had no effect on the accumulation of DNTEB. The change in the sensitivity of determination with changing pH can be explained by a change in the character and quantity of active adsorption sites at the GCE at different pHs and also by a change in both the adsorption activity of DNTEB at the electrode surface and the mechanism of its reduction. At pH < 3, aromatic nitro compounds are reduced in two stages, first to arylhydroxylamines



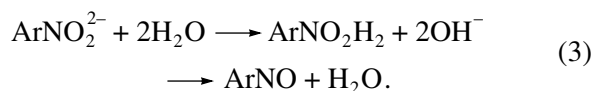
and further to corresponding amines [2, 5]. The two-stage process of DNTEB reduction is confirmed by the presence of two peaks in the voltammograms (Fig. 3). The peak at a less negative potential is suitable for analytical purposes. The symmetry of the peak is a criterion of the adsorption accumulation of DNTEB at the electrode surface [6]. At pH > 8, the reaction mechanism changed [2, 5] so that the first electrochemical stage in the electroreduction of the nitro group was the fast and reversible addition of two electrons, which resulted in the formation of a dianion:



The dianion was reversibly protonated and formed an unstable dioxonium compound, which irreversibly decomposed to give a nitroso compound:

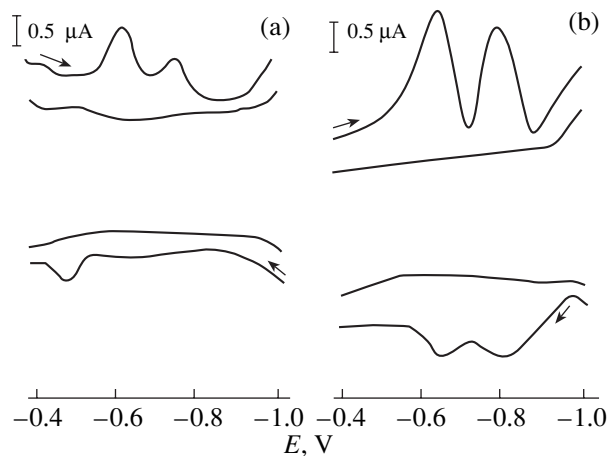


**Fig. 2.** Sensitivity of the cathodic voltammetric determination of DNTEB at a GCE as a function of the pH of the supporting electrolyte, (2 : 3)  $\text{C}_2\text{H}_5\text{OH-NH}_4\text{Cl}$  solution (analytical range,  $4.0 \times 10^{-5}$  to  $1.2 \times 10^{-3}$  M;  $E_{\text{acc}} = -0.4$  V;  $\tau_{\text{acc}} = 60$  s;  $v_{\text{sw}} = 7$  mV/s).

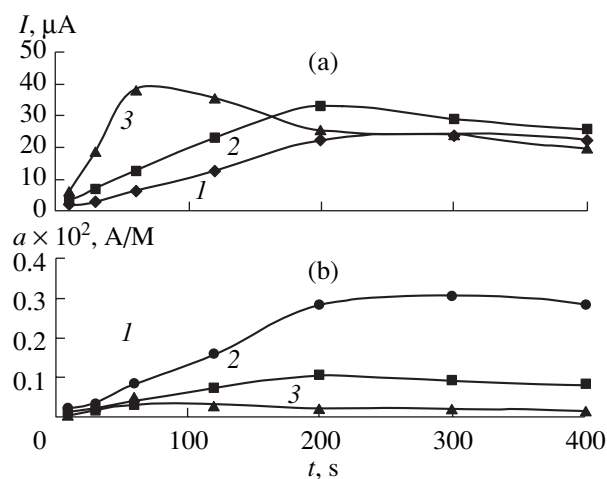


In this case, the adsorption behavior of DNTEB reduction products changed, which affected both the sensitivity and the precision of the voltammetric determination of DNTEB.

When the accumulation potential was changed from +0.1 to  $-0.6$  V, the maximum analytical signal was observed at  $E = -0.4$  V. At more negative potentials, the heights of peaks decreased, because DNTEB molecules adsorbed on the GCE surface were reduced during accumulation, and two peaks merged together (the first DNTEB peak flattened at the expense of an increase in the second peak).



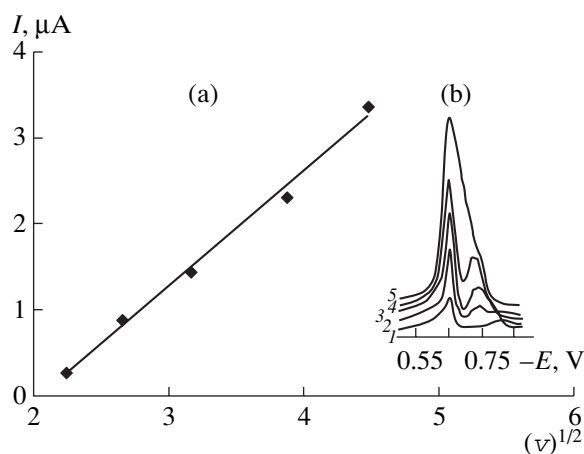
**Fig. 3.** Cathodic ( $E_{\text{acc}} = -0.4$  V) and anodic ( $E_{\text{acc}} = -1.4$  V) voltammograms of DNTEB ( $c = 4.00 \times 10^{-5}$  M) at (a) a GCE and (b) a MFE after a 60-s accumulation in a (2 : 3)  $\text{C}_2\text{H}_5\text{OH-NH}_4\text{Cl}$  solution at pH 4.



**Fig. 4.** (a) DNTEB peak current and (b) the sensitivity of its determination as functions of accumulation time (supporting electrolyte, (2 : 3)  $C_2H_5OH-NH_4Cl$  solution; pH 4;  $E_{acc} = -0.4$  V;  $v_{sw} = 7$  mV/s) in (1)  $7.92 \times 10^{-5}$ , (2)  $3.15 \times 10^{-4}$ , and (3)  $1.16 \times 10^{-3}$  M solutions.

The height of the cathodic peak was studied as a function of accumulation time in the range from 0 to 300 s at different concentrations of DNTEB (Fig. 4). Another corroboration of the adsorption nature of the accumulation of DNTEB on the GCE is an increase in sensitivity with decreasing DNTEB concentration at the same accumulation time (Fig. 4a) [6]. At concentrations of DNTEB higher than  $10^{-3}$  M and an accumulation time longer than 60 s, both the analytical signal and the sensitivity of determination decreased. Therefore, all experiments were carried out at an accumulation time of 60 s. At lower concentrations of DNTEB, it is advisable to prolong accumulation time to 200 s.

Figure 5 presents the analytical signal and voltammogram shape as functions of the rate of linear potential sweep. At a minimum rate of potential sweep, the only peak was observed in the voltammogram. The shape of the voltammogram became more complicated starting from a potential sweep rate of 7 mV/s. As the rate of potential sweep was increased, the heights of peaks grew and partially overlapped (superimposed), and, at a potential sweep rate of 50 mV/s, the peaks merged together. The best separated peaks were observed at a potential sweep rate of 7 mV/s. Regardless of the given rate of potential sweep, the potential of the first peak remained the same, which, together with



**Fig. 5.** (a) DNTEB peak current ( $c = 4.00 \times 10^{-5}$  M) as a function of potential sweep rate and (b) cathodic voltammograms of DNTEB at the GCE at different rates of potential linear sweep: 1, 5; 2, 7; 3, 10; 4, 15; and 5, 50 mV/s.

a proportionality of  $I_p$  to  $v^{1/2}$ , is a criterion of the reversibility of the electrochemical reduction of DNTEB at a GCE [6].

It is known that the analytical signal depends on the state of the electrode surface and the technique of its treatment [6–9]. The stability of GCE operation after single polishing was studied by the reproducibility of the shape of the voltammogram and the value of the analytical signal of DNTEB ( $I_p$ ) in its determination by voltammetry. The confidence limits for different concentrations were at most 13% after 74 measurements. The potential of the first peak of DNTEB remained unchanged.

Table 1 presents the parameters of the DNTEB peak current as a function of its concentration in the range from  $4.0 \times 10^{-3}$  to  $3.0 \times 10^{-3}$  M. These parameters show that both MFE and GCE can be used in the voltammetric determination of DNTEB in cathodic and anodic branches of voltammograms. However, the narrow linearity range of the MFE lowers its performance. The calibration graph obtained for the GCE operated in the anodic mode was linear in the entire analytical range, but the sensitivity of determination was three times lower than that obtained at the GCE in the cathodic mode. Based on our studies, we developed a procedure for the voltammetric determination of DNTEB at a

**Table 1.** Parameters of DNTEB peak current as a function of its concentration in the voltammetric determination of DNTEB

Direction of linear potential sweep	Electrode	Linearity range $\times 10^5$ , M	$I = a \times 10^2 c + b \times 10^6$	R
Cathodic	GCE	4–120	$2.17c + 5.20$	0.991
	MFE	4–16	$7.43c + 2.62$	0.992
Anodic	GCE	4–260	$0.80c + 1.77$	0.974
	MFE	4–28	$3.16c + 1.63$	0.995

**Table 2.** Determination of DNTEB in reaction mixtures by polarography and voltammetry ( $n = 5, P = 0.95$ )

Polarographic determination of DNTEB		VA determination of DNTEB		$S^2 \times 10^5$	$t_{\text{exp}} \times 10^2$	$F_{\text{exp}}$
$(X_{\text{pol}} \pm c) \times 10^4, \text{M}$	$S \times 10^5$	$(X_{\text{VA}} \pm c) \times 10^4, \text{M}$	$S \times 10^5$			
$3.16 \pm 0.48$	3.83	$3.31 \pm 0.10$	0.76	2.23	0.50	5.05
$3.39 \pm 0.10$	0.80	$3.56 \pm 0.16$	1.28	1.65	0.66	1.59
$2.80 \pm 1.69$	13.58	$4.98 \pm 1.09$	8.75	11.20	3.25	1.55

GCE (supporting electrolyte, (2 : 3)  $\text{C}_2\text{H}_5\text{OH} : \text{NH}_4\text{Cl}$ ; accumulation time, 60 s; accumulation potential,  $-0.4 \text{ V}$ ; rate of potential sweep,  $v_{\text{sw}} = 7 \text{ mV/s}$ ; and pH 4).

Table 2 presents the results of analysis of a real sample, an intermediate product in the production of polyurethane foam (a methanolic–ethanolic solution of DNTEB and diaminotriethylbenzene). The concentration of DNTEB in the product was found by the standard addition method. The results obtained by voltammetry ( $X_{\text{VA}}$ ) were compared with those obtained by classical polarography using a PU-1 polarograph ( $X_{\text{pol}}$ ) in the chemical laboratory of ZAO Spektr-Khimtek (Kemerovo). Because  $F_{\text{tab}}(4; 4) = 6.4 > F_{\text{exp}}$ , the discrepancy between the variances was insignificant and, therefore, the methods are equally accurate. A comparison of the average values of  $X_{\text{pol}}$  and  $X_{\text{VA}}$  using the  $t$  test ( $t_{\text{exp}} < t_{\text{tab}}$ ) showed that both samples belong to the same statistical population.

The results obtained indicate that the developed procedure can be recommended for the analysis of compounds containing DNTEB.

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