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Electrochemical Determination of Some Triphenylmethane Dyes by Means of Voltammetry

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Abstract

This paper provides the investigation of electrochemical properties of triphenylmethane dyes using a voltammetric method with constant-current potential sweep. Malachite green (MG) and basic fuchsin (BF) have been chosen as representatives of the triphenylmethane dyes. The electrochemical behavior of MG and BF on the surface of a mercury-film electrode depending on pH, the nature of background electrolyte and scan rate of potential sweep have been investigated. The conditions of registration have been determined for MG and BF detecting in the solution. It is demonstrated that the reduction peak currents of MG and BF increase linearly with their concentration in the range of $9.0 \cdot 10^{-5}$ – $7.0 \cdot 10^{-3}$ mol/dm³ for MG, $6.0 \cdot 10^{-5}$ – $8.0 \cdot 10^{-3}$ mol/dm³ for BF with correlation coefficients of 0.9987 and 0.9961, respectively. The detection limit of MG is $5.0 \cdot 10^{-5}$ mol/dm³ and for BF - $2.0 \cdot 10^{-5}$ mol/dm³.

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1. Introduction

The exclusive use of dyes mineral, plant, or animal derived materials covers the period starting from the origin of mankind and up to 1859. Application of artificial colors began with the mauveine discovery in 1856. Triphenylmethane dyes are among the first synthetic dyes, they still retain a great value in various fields of human activity¹. The range of application of this class of dyes is very wide, they are used mainly for dyeing silk, cotton,

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leather and paper; moreover, as acid-base indicators some of them possess potent anti-fungal, anti-bacterial and anti-parasitic properties, thereby, they are applied in medicine. To date, triphenylmethane dyes can be classified into three main groups: 1) dyes of malachite green group (with two amino groups in a molecule); 2) dyes of rosaniline group (with three amino groups in a molecule); 3) dyes of rosolic acid group (with three hydroxyl groups in a molecule)².

In this paper the electrochemical properties of triphenylmethane dyes, representatives of 1 and 2 groups, namely malachite green and basic fuchsin have been studied; structural formulas of them are represented in Figure 1.

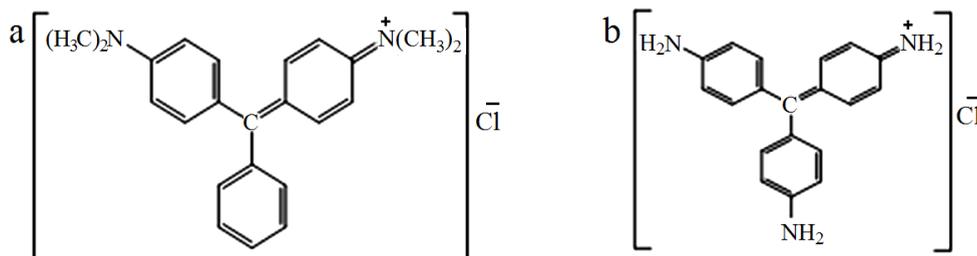


Fig.1. Structural formulas of MG (a) and BF (b)

The studies on the electrochemical properties of the triphenylmethane dyes were previously performed^{3,4,5}. The greatest interest for the study is represented in the works about electrochemistry of malachite green and fuchsin. So, for example, the authors⁶ studied the electrochemical behavior of MG glassy carbon electrode and its interaction with DNA for subsequent detection of DNA on the electrode modified by MG; in the research⁷ the electrochemical study of MG using the iron electrode was performed; moreover there is a work on the preparation of poly malachite green film on the surface of carbon electrodes with the further use of such electrodes to determine dopamine, NADH and ascorbic acid^{8,9}; Jia-Yi Chen with colleagues carried out a joint determination of DNA bases using the new graphene electrode, which was electrochemically modified by fuchsin¹⁰.

The study of the electrochemical behavior of MG and BF on the surface of a mercury-film electrode was performed with the view of further identification in different objects, and also to prove the possibility of MG and BF application as sensors for electrochemically inactive compounds which were complexable with cationic dyes. In contrast to the previously known works, in the presented paper the studies were carried out on the surface of a mercury-film electrode using an aqueous background electrolyte; the electroreduction of MG and BF was investigated; and also analytical parts (range of linear dependence I μA on concentration mol/dm³, a detection limit) were estimated for quantitative detection of the studied dyes in simulated solutions.

2. Materials and methods

When studying the electrochemical properties of triphenylmethane dyes the current-voltage curves were recorded by means of voltammetric analyzer TA-2 («Tomanalyt», Tomsk). The measurements were carried out in a three-electrode electrochemical cell in which the mercury-film electrode (MFE) acted as an indicator electrode, a silver chloride electrode (Ag/AgCl/KCl, 1M) was used as a reference electrode, a platinum electrode was used as an auxiliary electrode. The indicator MFE was on preliminary polarization in the field of potentials from 0.0 V to -2.0 V by cyclic voltammetry with a scan rate of 60mV/sec for 10 cycles for the experimental error decrease. The analyzer Itan (pH-meter/ionomer) was used to measure pH. All experiments were carried out at a room temperature.

Dye solutions were prepared for MG with a “pure for analysis” classification (content of colorant > 90%) of China production, and BF with a “for microbiological purposes” classification (colorant content not less than 88%) of Russia production. The MG dye solution was prepared by dissolving 0.1825±0.0002 g of its sample in 50 ml of bidistilled water. Due to the fact that fuchsin is poorly soluble in water, its solution was prepared by dissolving 0.08447 ± 0.0002 g of a dye sample in 25 ml of 96% ethanol. The prepared solutions of the triphenylmethane dyes were stored in dark glass chemical dish at a room temperature.

The investigation of electrochemical properties of nitrogenous bases was carried out with the use of background

solutions having different values of pH. A set of standard titres was used for the preparation of aqueous background solutions with the specified value of pH, working standards of the third category:

- pH 1.65 - potassium tetraoxalate, 0.05M $\text{KH}_3\text{C}_4\text{O}_8 \cdot 2\text{H}_2\text{O}$;
- pH 4.01 – potassium hydrogen phthalate, 0.05M $\text{KC}_8\text{H}_5\text{O}_4$;
- pH 6.86 – potassium phosphate monobasic 0.025M KH_2PO_4 , sodium phosphate dibasic 0.025 M Na_2HPO_4 ;
- pH 9.18 – sodium tetraborate, 0.01 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$;

A Britton-Robinson universal buffer solutions with pH from 1.95 till 11.6 (0.04 M solution of phosphoric and acetic and boric acids with addition of a certain volume of 0.2 M NaOH) were used to carry out the research.

Other chemicals were of analytical reagent grade and were used without further purification.

3. Results and discussion

The electrochemical properties of MG and BF were investigated by cyclic and cathodic voltammetry with constant-current potential sweep on a mercury-film electrode.

Figure 2 shows the cyclic voltammograms of MG and BF in a potassium tetraoxalate buffer solution (0.05M $\text{KH}_3\text{C}_4\text{O}_8 \cdot 2\text{H}_2\text{O}$) with pH=1.65.

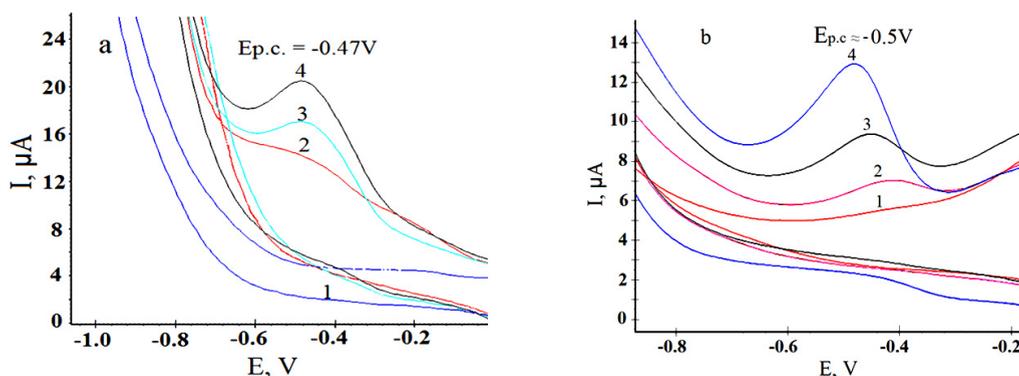


Fig.2. Cyclic voltammograms of MG (a), BF (b) on MFE: 1-background curve; 2 - $C_{\text{MG}} = 5.0 \cdot 10^{-4} \text{ mol/dm}^3$, $C_{\text{BF}} = 2.0 \cdot 10^{-3} \text{ mol/dm}^3$; 3 - $C_{\text{MG}} = 1.0 \cdot 10^{-3} \text{ mol/dm}^3$, $C_{\text{BF}} = 5.0 \cdot 10^{-3} \text{ mol/dm}^3$; 4 - $C_{\text{MG}} = 2.0 \cdot 10^{-3} \text{ mol/dm}^3$, $C_{\text{BF}} = 8.0 \cdot 10^{-3} \text{ mol/dm}^3$. pH= 1.65, W = 60 mV/sec.

MG and BF on MFE were electrochemically active only in a cathodic area according to the data presented in Figure 2. A cyclic voltammogram demonstrated that only MG and BF electroreduction peaks indicated that the electrochemical process under selected conditions was, most likely, totally irreversible. All further studies on the electrochemical properties of MG and BF presented in this work were carried out by cathodic voltammetry in the potential range from -0.1 V to -1.5 V. The investigated solution of a background electrolyte of 10 cm³ was placed in an electrochemical cell and mixed with nitrogen using a noble gas (to remove the interfering effect of oxygen on the received signal).

Besides two electrons two protons (2H^+) participate in the process of electroreduction of MG and BF^{11,12}. Due to that there is a possibility to conclude that the value of supporting electrolyte pH is an important parameter in this case that can affect redox behavior of the studied substances. Therefore, the effect of pH on the reduction response of MG and BF has been investigated by cathodic voltammetry in buffer solutions with the pH range from 1.65 to 9.18 (Figure 3).

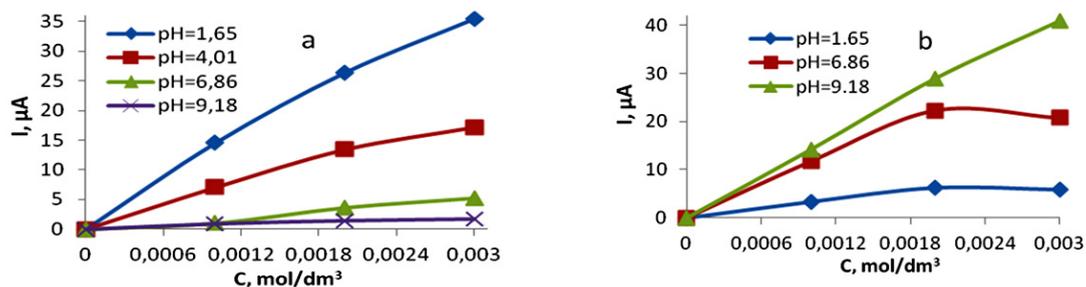


Fig.3. Dependence of current of MG (a) and BF (b) electroreduction on their concentration on MFE at different pH values

Figure 3 shows that the maximum value of currents for MG is observed at pH=1.65, whereas for fuchsin the maximum value of currents is recorded in sodium tetraborate buffer solution with pH=9.18.

To exclude the influence of the background electrolyte nature on a signal of MG voltammetric curves were recorded in a universal Britton-Robinson buffer solution with pH from 1.95 to 11.6. The dependences of signals intensity and changes of potential peaks of MG on pH were constructed according to the obtained data (Figure 4).

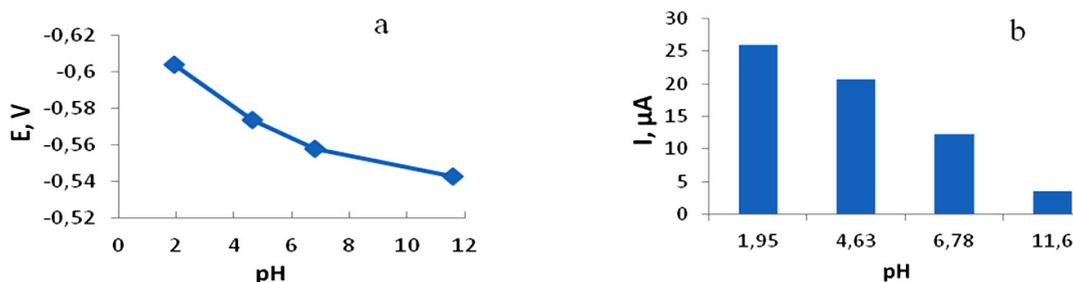


Fig.4. Dependence of reduction potential peak (a) and current of electroreduction of MG on the MFE on pH of the Britton-Robinson buffer solution. $C_{\text{MG}}=1.0 \cdot 10^{-3} \text{ mol/dm}^3$.

It can be seen from Figure 4 that when supporting electrolyte pH changes from the acidic medium (pH = 1.95) to alkaline one (pH = 11.6), there is a shift of potential in more positive area. Considering that the reaction proceeds only in the forward direction based on the Nernst equation, the increasing number of protons increases the yield of the reduced form of MG. This results in a shift of the potential to more positive area at the pH medium change from acidic to alkaline.

The maximum value of currents of MG electroreduction is observed in background electrolytes with acidic pH, while in neutral and alkaline media the signal intensity of MG decreases (Figures 3a and 4b). It can be explained by the fact that, in the acidic medium, MG is in more active protonated form¹³ (Figure 5).

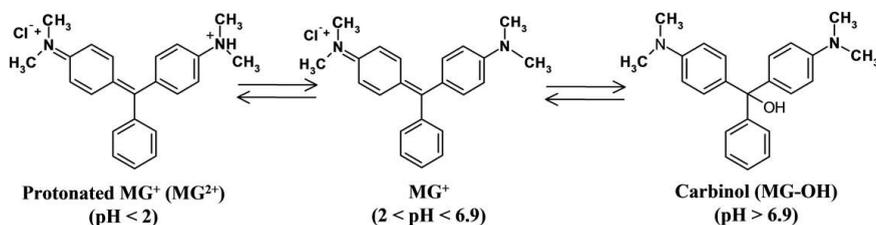


Fig.5. Scheme of pH effect on the MG structure in aqueous solutions

Further, to exclude the influence of the background electrolyte nature on a signal of BF, its electrochemical behavior was investigated in a Britton-Robinson solution. The voltammetric curves were recorded in a pH range

from 1.95 to 9.27; the dependences of signals intensity on pH and the changes of potential peaks of BF were constructed according to the obtained data (Figure 6).

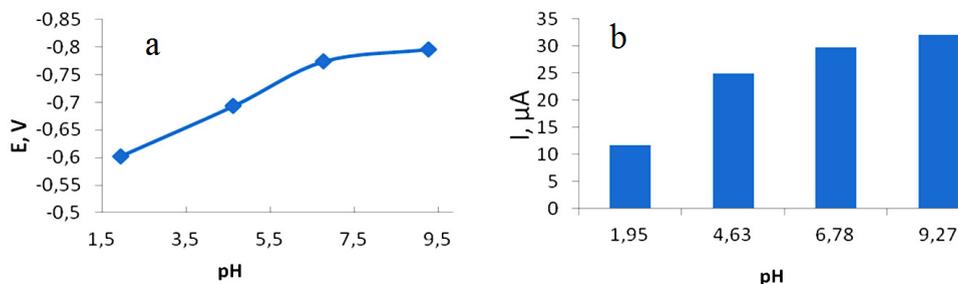


Fig.6. Dependences of reduction potential peak (a) and BF electroreduction current on the MFE on pH of the Britton-Robinson buffer solution. $C_{BF}=2.0 \cdot 10^{-3} \text{ mol/dm}^3$

There is a larger number of hydrogen protons involved in the process of MG electroreduction in an acidic medium than in alkaline one and, as a result, it leads to increasing the value of the potential, and therefore, to its shift in more positive area with the change in pH from alkaline to an acidic medium (Figure 6a). According to the data presented in Figures 3b and 6a the maximum value of currents of BF electroreduction is observed at alkaline pH. It can be explained by the fact that fuchsin is in the basic form, which is the most active in solutions with alkaline pH.

On the basis of the above data, it is possible to assume that for determination of MG on MFE more appropriate pH value of the supporting electrolyte is $\text{pH} = 1.65$, and for BF $\text{pH}=9.18$.

The influence of the scan rate on the reduction peak currents of MG and BF was investigated in the range from 30 to 300 mV/sec in potassium tetraoxalate background solution with $\text{pH}=1.65$ for MG and sodium tetraborate with $\text{pH}=9.18$ for BF. The study of the influence of the scan rate (W) on the electroreduction peaks of MG and BF demonstrated that the intensity signal increased for MG with gradually increasing W , whereas for BF the value of current reached the maximum at $W=120$ mV/sec and at the subsequent increase of W the current decreased. So, the peak currents of $1.0 \cdot 10^{-3} \text{ mol/dm}^3$ of MG in electrochemical cell showed a linear increase with a square root of square wave frequency, suggesting that the electrode reactions for the reduction of MG was a diffusion controlled process. With reference to the obtained data it was possible to assume that the optimal scan rate of potential sweep for MG was 180mV/sec, and 120mV/sec for BF to receive more intensive, stable, reproducible signals of electroreduction of the studied dyes.

The cathodic voltammograms were recorded to create calibration curves for varying concentrations of MG and BF. The received data allowed constructing the dependences of currents electroreduction of MG in a potassium tetraoxalate background solution with $\text{pH}=1.65$ at $W=180$ mV/sec and BF in a sodium tetraborate buffer solution with $\text{pH}=9.18$ at $W=120$ mV/sec (Figure 7).

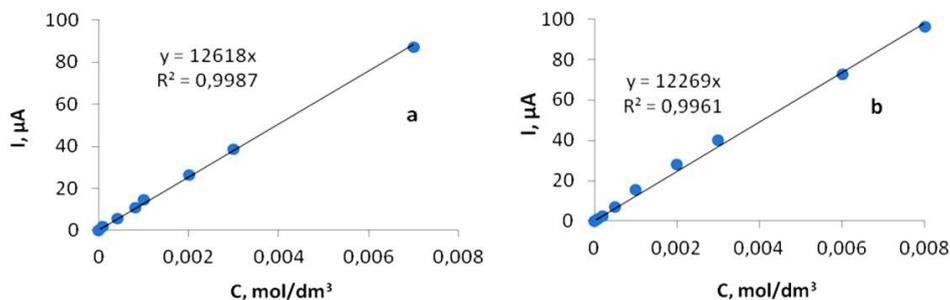


Fig.7. Dependence curves of currents of MG (a) and BF (b) reduction on their concentration in the electrochemical cell

Figure 7 reveals that the reduction peak currents of MG and BF increases linearly with their concentration in the

range of $9.0 \cdot 10^{-5}$ – $7.0 \cdot 10^{-3}$ mol/dm³ for MG, $6.0 \cdot 10^{-5}$ – $8.0 \cdot 10^{-3}$ mol/dm³ for BF with correlation coefficients of 0.9987 and 0.9961, respectively. The detection limit of MG is $5.0 \cdot 10^{-5}$ mol/dm³ and for BF $2.0 \cdot 10^{-5}$ mol/dm³.

4. Conclusions

In this work the influence of the pH, nature of background electrolyte and scan rate of potential sweep on the electrochemical behavior of the MG and BF triphenylmethane dyes has been investigated. According to the research the potassium tetraoxalate background solution with pH equal to 1.65 at the scan rate of 180 mV/sec has been chosen as an optimal value for the MG determination on the MFE and sodium tetraborate buffer solution with pH=9.18 at W=120 mV/sec for the BF detection. The increase of reduction peak currents is proportional to concentration of MG in the range from $9.0 \cdot 10^{-5}$ to $7.0 \cdot 10^{-3}$ mol/dm³ ($R^2=0.9987$) and BF from $6.0 \cdot 10^{-5}$ to $8.0 \cdot 10^{-3}$ mol/dm³ ($R^2=0.9961$) under optimal conditions. The detection limit of MG is $5.0 \cdot 10^{-5}$ mol/dm³ and BF - $2.0 \cdot 10^{-5}$ mol/dm³. Also, the electrochemical system presented in this paper and having in its composition MG dye has been successfully applied for the indirect determination of heparin in pharmaceuticals¹⁴.

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References

1. Gaupman Z., Grefe Yu., Pemane H. *Organic chemistry*. Chemistry, Moscow, 1979. (In Russian)
2. Karrer P. *The course of organic chemistry*. Translated from German. L.: State scientific and technical publishing house of chemical literature, 1960. (In Russian).
3. Hall DA., Sakuma M. and Elving PJ. Voltammetric Oxidation of Triphenylmethane Dyes at Platinum in Liquid Sulphur Dioxide. *Electrochimica Acta*. 1966; **11**: 337 – 350.
4. Chun Hin Ng, C. Andre Ohlin, Bjorn Winther-Jensen. Characterisation of a series of triarylmethane dyes as light harvesters for photo-electrochemical systems. *Dyes and Pigments*. 2015; **115**: 96-101
5. Kobotaeva NS, Sirotkina EE, Mikubaeva EV. Electrochemical oxidation of tritane dyes. *Journal of Electrochemistry*. 2006; **42**, Issue 3: 268-271
6. Xuan Hu, Kui Jiao, Wei Sun, Jia-Yu You. Electrochemical and Spectroscopic Studies on the Interaction of Malachite Green with DNA and Its Application. *Electroanalysis*. 2006; **18**, **6**: 613 – 620.
7. Seema Singh, Vimal Chandra Srivastava, Indra Deo Mall. Electrochemical Treatment Of Malachite Green Dye Solution Using Iron Electrode. *International Journal of ChemTech Research*. 2013; **5**, **2**: 592-596.
8. Shen-Ming Chen, Ji-Yan Chen, R. Thangamuthu. Electrochemical Preparation of Poly(Malachite Green) Film Modified Nafion-Coated Glassy Carbon Electrode and Its Electrocatalytic Behavior Towards NADH, Dopamine and Ascorbic Acid. *Electroanalysis*. 2007; **19**, **14**: 1531 – 1538.
9. Qijin Wan, Xiaoxia Wang, Xing Wang, Nianjun Yang. Poly(malachite green) film: Electrosynthesis, characterization, and sensor application. *Polymer*. 2006; **47**: 7684-7692.
10. Jia-Yi Chen Shen-Ming Chen, Wen-Hui Weng, Ying Li, Shaoh-Der Yeh. Simultaneous Detection of DNA Bases on Electrodes Chemically Modified with Graphene-New Fuchsin. *Int. J. Electrochem. Sci*. 2013; **8**: 3963 – 3973.
11. Gosta Bengtsson. Polarographic Studies of Basic Triarylmethane Dyes. Kinetics, Equilibria and Behavior of Malachite Green in Aqueous Solutions. *Acta Chemica Scandinavica*. 1967; **21**: 2544-2558.
12. Shen-Ming Chen, Yu-Hsiang Fa. The electropolymerization and electrocatalytic properties of polymerized new fuchsin film modified electrodes. *Journal of Electroanalytical Chemistry*. 2003; **553**: 63- 75.
13. Nguyen M. Cuong, Shoji Ishizaka, Noboru Kitamura. Donnan Electric Potential Dependence of Intraparticle Diffusion of Malachite Green in Single Cation Exchange Resin Particles: A Laser Trapping-Microspectroscopy Study. *American Journal of Analytical Chemistry*. 2012; **3**, **3**: 188-194.
14. Vishenkova DA., Korotkova EI., Dorozhko EV. Electrochemical determination of heparin in pharmaceuticals with using malachite green. *Advanced Materials Research*. 2014; **1040**: 292-296.