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Optical and Raman Experiments for the Electro-organic Synthesis of Bromothymol Blue and Bromophenol Blue

Achim Habekost[*]

Department of Chemistry Didactics, University of Education, Ludwigsburg, Germany
*Corresponding author: A.Habekost@t-online.de

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Abstract Recently, a Journal of Chemistry Didactics claimed that bromothymol blue and bromophenol blue could be prepared in situ by oxidation of bromide to bromine, which subsequently reacts with thymol blue and phenol red, respectively. The hypothesis has now been unequivocally confirmed by absorbtovoltammetry and Raman voltammetry. The substitution of bromine by bromide is an important contribution to experiments with less hazardous materials in chemistry education. In Germany, students are not allowed to experiment with bromine. On the other hand, there are many experiments that use bromine. Therefore, the in situ electrochemical generation of bromine from bromide can be a good alternative in terms of green chemistry.

Keywords: *Ramanspectroscopy, Electrochemistry, Electro-organic Synthesis*

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1. Introduction

The Trend Report section of the German chemistry journal "Nachrichten aus der Chemie" recently highlighted the diverse possibilities of electro-synthesis - from (enantioselective) cross-coupling of carboxylic acids to the production of strong oxidising agents and the formation of Si-Si bonds [1]. However, despite their enormous importance, electro-organic syntheses have so far played a rather subordinate role in experimental chemistry teaching. The main reason for this is the need to find electro-organic reactions that can be characterised using the tools of school chemistry [2]. Using absorption and fluorescence spectroscopy and thin-layer chromatography, Lanfermann et al [3] described the formation of eosin by electrobromination from bromide and fluorescein. Ducci [4,5] described the analogous preparation of bromothymol blue and bromophenol red from thymol blue and phenol red, respectively, and of eosin from fluorescein. The main aim of this work was to replace bromine as an educt by the in-situ generation of bromine by electrooxidation of bromide salts. This eliminates the need for initial handling of bromine to carry out the reaction. The hazardous bromine should not be used in chemistry education. However, there are many reactions in inorganic and organic chemistry, e.g. redox reactions, substitution reactions, etc., that can probably be modified by primary oxidation of bromide to produce bromine. In addition to a double bromination of thymol blue and phenol red, Ducci also suggests a multiple bromination with a longer electrolysis time, which leads to a decolourisation of the respective solutions.

To prove these assumptions, we have used absorpto- and Ramanvoltammetry and show that the electro-organic synthesis of bromothymol blue and bromophenol blue proceeds according to a non-catalytic mechanism from about 0.9 V from molecular bromine produced in-situ. At longer electrolysis times, products are formed, presumably by reaction with more bromine and/or with electrolytically produced oxygen. More detailed studies of this are awaited.

The experiments described here are not intended for school use, but for a university laboratory course.

2. Experiments

Equipment and chemicals: Potentiostat PGSTAT 204 (Metrohm), fiber spectrometer AvaSpec-ULS2048XL-EVO-RS-UA (Avantes), Raman spectrometer AvaRaman (Avantes), light source AvaLight-DH-S-BAL (Avantes), bifurcated fiber BFY 200HS02, 200-1200 nm (Thorlabs). Screen-printed electrodes: DRP 550 (Pt as working and counter electrode, Ag as reference electrode), DRP 010 (Ag as working electrode, C as counter electrode, Ag as reference electrode), DRP 250 Au-Bt (Au as working electrode, Au as counter electrode, Ag as reference electrode), DRP 110 CNT (carbon nanotubes as working electrode, C as counter electrode, Ag as reference electrode. Thin-film cell with electrodes (Metrom/DropSens)

Software: DropView (DropSens/Metrohm), AvaSoft (Avantes) and Spectragryph (Dr. Menges).

Thymol blue Na salt (EC no. 263-650-6, Carl Roth, no H and P phrases), bromothymol blue (17778.0801, Analytics Bernd Kraft, HP phrases P 280.1-3+5), bromophenol blue (20091.0801, Analytics Bernd Kraft, no H and P phrases), phenol red (EC no. 205-609-7, Carl Roth, H: 315-335, P: 261-264-271-280-302+352-304+340+312), KCl (EC no. 231-211-8, Carl Roth, no H and P phrases), KBr (EC no. 231-830-3, Carl Roth, H: 319, P: 305+351+338).

Solutions: 0.1 mmol of the substance under investigation in 1 mmol KCl as the conducting salt. Addition of 0.1 mmol KBr solution. In each case 60 µL solution was used (10 µL substance, 10 µL KBr solution, 40 µL KCl solution).

Absorptovoltammetry

Thymol blue / bromothymol blue

Thymol blue and bromothymol blue are commonly used as pH indicators in analytical chemistry. The colour varies from yellow-orange to blue-green depending on the pH. The measurements shown in this article were made at pH = 6. Figure 1 shows the reaction from thymol blue to bromothymol blue. Bromine is typically generated electrochemically at the anode when a bromide ion (Br^-) solution is subjected to oxidation. At the electrode surface, bromide ions lose electrons to form bromine (Br_2) or bromine radicals (Br•). The generated bromine species (Br_2 or Br•) can then act as an electrophile in the next step. The bromine radical (Br•) or bromine molecule can form a bromonium ion intermediate or directly react with thymol blue. The bromination usually occurs at positions on the aromatic ring where electron density is available, often at the ortho or para positions relative to electron-donating groups (like hydroxyl or methoxy groups) on the thymol blue structure. After the electrophilic attack, a brominated thymol blue derivative is formed. The specific position of bromination depends on the structure and the conditions of the electrochemical reaction. One product, perhaps the most important, is bromothymol blue.

An analogous reaction is the bromination of phenol red to bromophenol blue (see Supporting Information, figure S1).

Figure 2 shows the absorption spectra of thymol blue (solid line) and bromothymol blue (dashed line). There is only a relatively small spectral shift of the absorption spectra of the substances of about 20 nm and a broad overlap. The absorption spectra of phenol red and bromophenol blue are given in the Supporting Information, figure S2.

Absorptovoltammograms were performed using a thin-film quartz cuvette. Inside the cuvette (2 mm thickness) is a platinum grid as the working electrode, an Ag/AgCl as the reference and a platinum grid as the counter electrode (Figure 3).

The three-dimensional absorptovoltammogram (absorption as a function of wavelength and the applied potential) in Figure 4 shows the growth of bromothymol blue absorption, which begins at approx. 0.85 V. The standard potential for the reaction $Br_2 + 2e^- \rightleftharpoons 2\ Br^-$ is 0.84 V relative to the standard potential for Ag/AgCl (0.22 V).

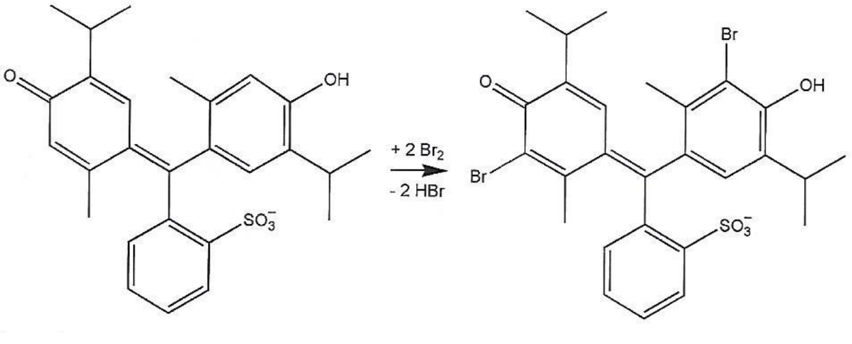


Figure 1. Reaction scheme of the bromination of thymol blue (left) to bromthymol blue (right)

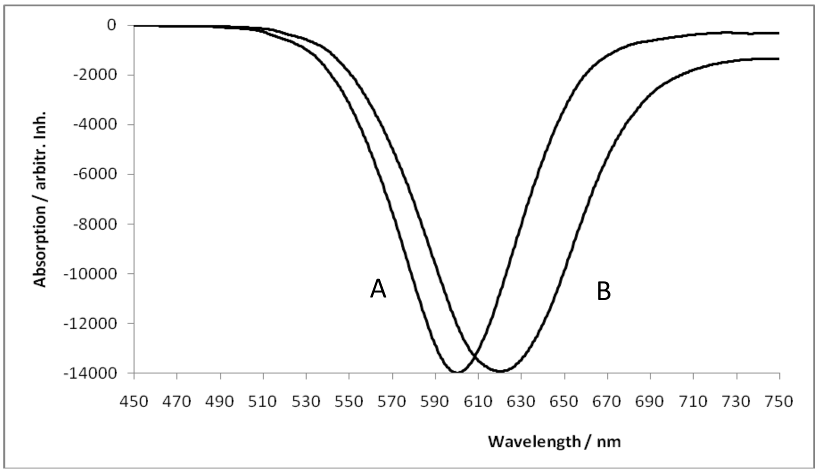


Figure 2. Change of the light intensity at pH=6. A: thymol blue, B: bromothymol blue

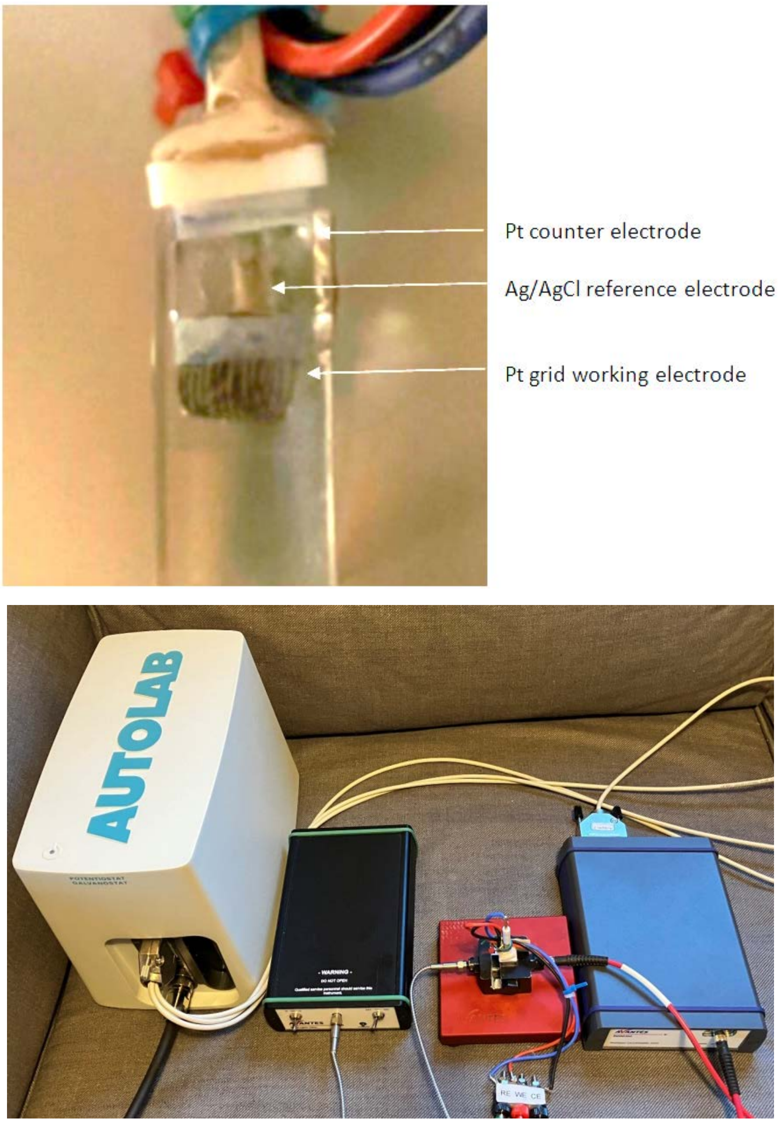


Figure 3. Top: Thin-film transmission quartz cell with Pt grid as working electrode, Ag/AgCl as reference electrode and Pt as counter electrode. Bottom: Experimental set-up for absorptovoltammetry. From left to right: Potentiostat with connection to the electrodes and trigger cable for triggering the fibre spectrometer, light source (halogen and deuterium light), quartz cell in the cell holder, fibre spectrometer. Fibre connection via two fibres: Light source - cell - fibre spectrometer.

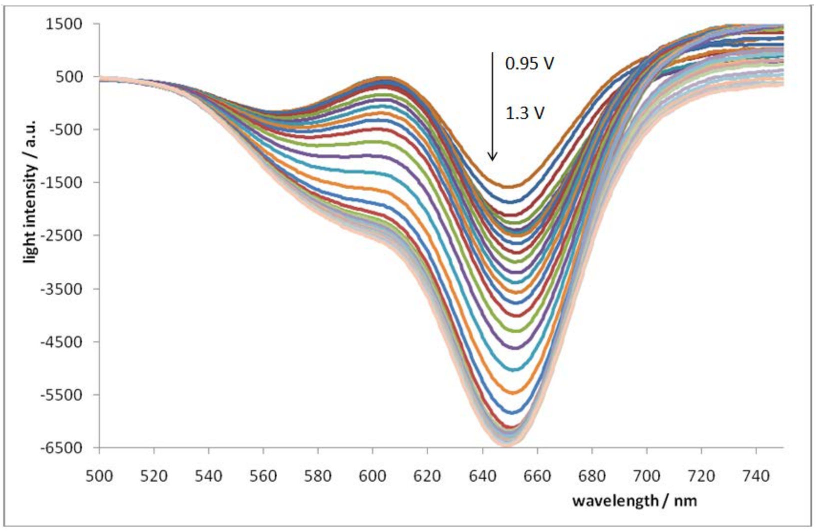


Figure 4. Change in the light intensity of thymol blue / bromide as a function of the applied potential from 0.95 V to 1.3 V.

The corresponding absorption voltammogram between 500 and 670 nm for the potential scan from 0.95 V to 1.3 V is shown in Figure 4. At approximately 0.85 V, the current flow increases and the light intensity between 610 and 650 nm decreases: The resulting bromothymol blue absorbs the corresponding light.

The inset in Figure 5 clearly shows the correlation between the current flow due to the oxidation of Br^- and the (negative) change in light intensity (derived absorptovoltammogram).

Phenol red shows an analogous behaviour, as the formation of bromophenol blue ((λmax = 600 nm) also starts at a potential of 0.85 V (see, Supporting Information S3).

It is therefore likely that the formation of bromothymol blue (and bromophenol blue) is directly related to the oxidation of bromide to bromine.

3. Raman Voltammetry

Unlike IR spectroscopy, Raman spectroscopy is a rather insensitive method that often requires longer integration times. However, its main advantage is its insensitivity to water, as it operates in the visible optical range (typically at 530 or 785 nm or in the IR range at 1.06 µm), where water does not absorb [6].

However, Surface Enhanced Raman Spectroscopy (SERS) can significantly increase the sensitivity of the measurement [6,7].

SERS is usually performed using Au or Ag nanoparticles prepared by methods described in the literature [8]. Experimentally, however, it is much easier to generate the nanoparticles directly on the Au or Ag electrode by electrochemical cyclisation [9,10]. For this purpose, we used the Ag SPE onto which a KCl solution (approximately 60 µL) was dripped so that all three electrodes were wetted. A cyclic voltammogram was then run three times between -0.6 V and +0.6 V and back. At approximately 0.3 V, Ag oxide forms on the Ag surface (as indicated by the darkening of the electrode). At -0.3 V, the Ag-O surface is reduced again to form the nanostructured surface [10].

Figure 6 shows the experimental set-up with the Raman probe inside the Raman cuvette with the so prepared SPE, figure 7 shows the SERS spectrum of thymol blue and figure 8 shows the SERS spectrum of bromothymol blue on the prepared Ag electrode.

The SERS Spectra of phenol red and bromophenol red is shown in the Supporting Information (S4 and S5).

For better comparison, a Raman spectrum of thymol blue and bromothymol blue is shown in figure 9. In addition to the differences in the intensity of the individual Raman transitions, it is noticeable that the Raman transitions at about 600 and 900 cm^{-1} occur only in the case of bromothymol blue (see arrow).

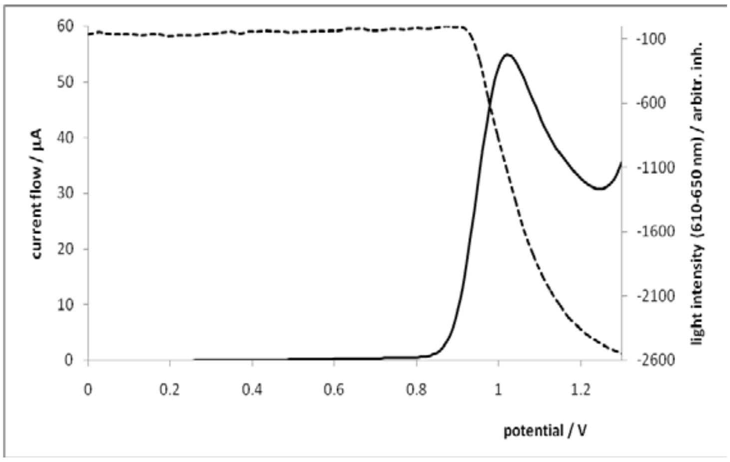


Figure 5. Absorptovoltammogram of thymol blue / bromide. Solid line: linear sweep voltammogram (LSV), dashed line: light intensity at 610 nm - 650 nm. Insert: LSV and derived light intensity

Figure 6. SERS set-up. From left to right: Raman spectrometer with 785 nm laser, Raman probe with Raman cell. Inside the Raman cell: SPE with connection to potentiostat (right). The potentiostat triggers the Raman spectrometer

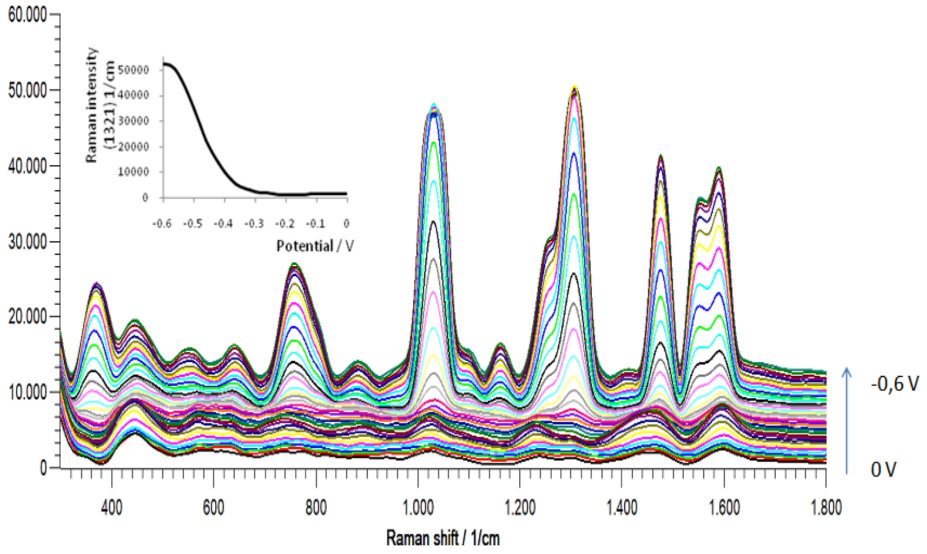


Figure 7. SERS of thymol blue between 0 and -0.6 V. Insert: Potential-dependent intensity of the transition at 1321 cm^{-1}

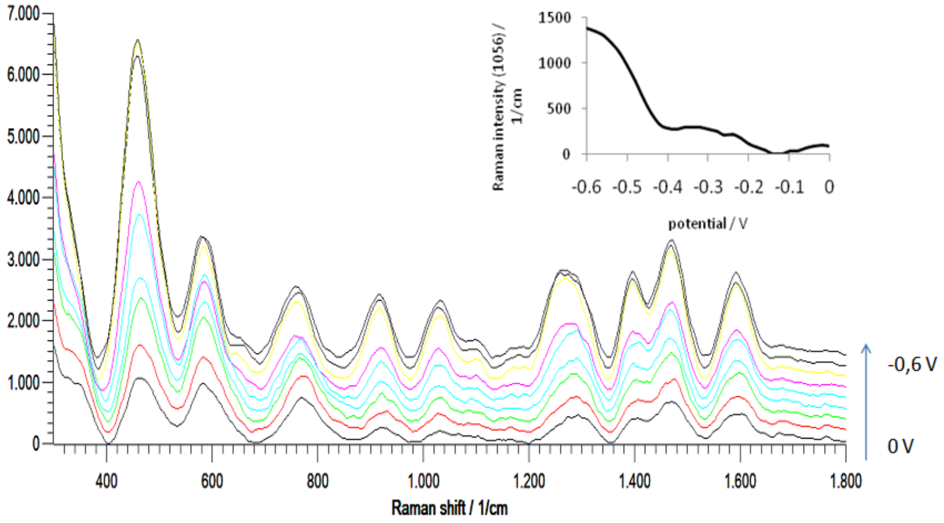


Figure 8. SERS bromothymol blue between 0 V and -0.6 V. Insert: Potential-dependent intensity of the transition at 1056 cm^{-1}

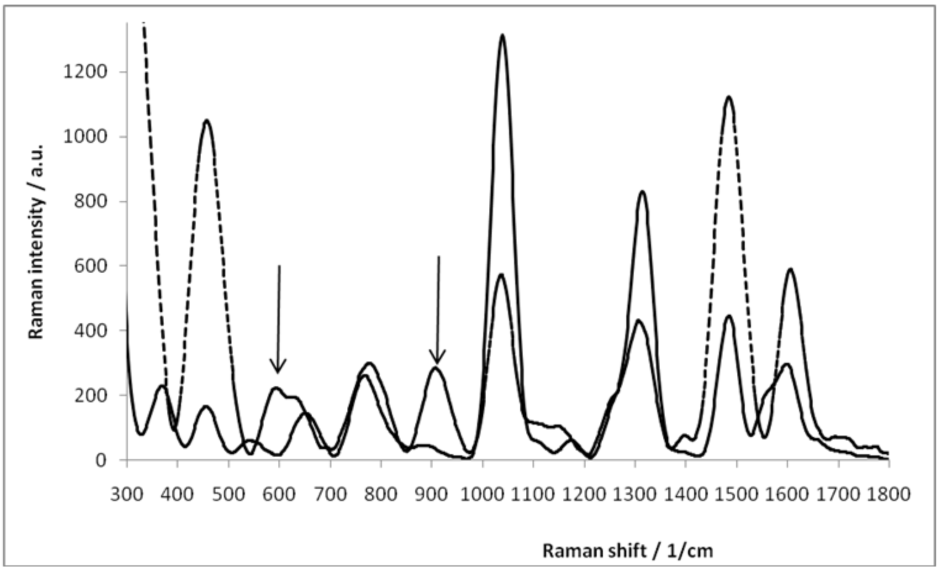


Figure 9. Raman spectra of thymol blue (solid line) and bromothymol blue (dashed line)

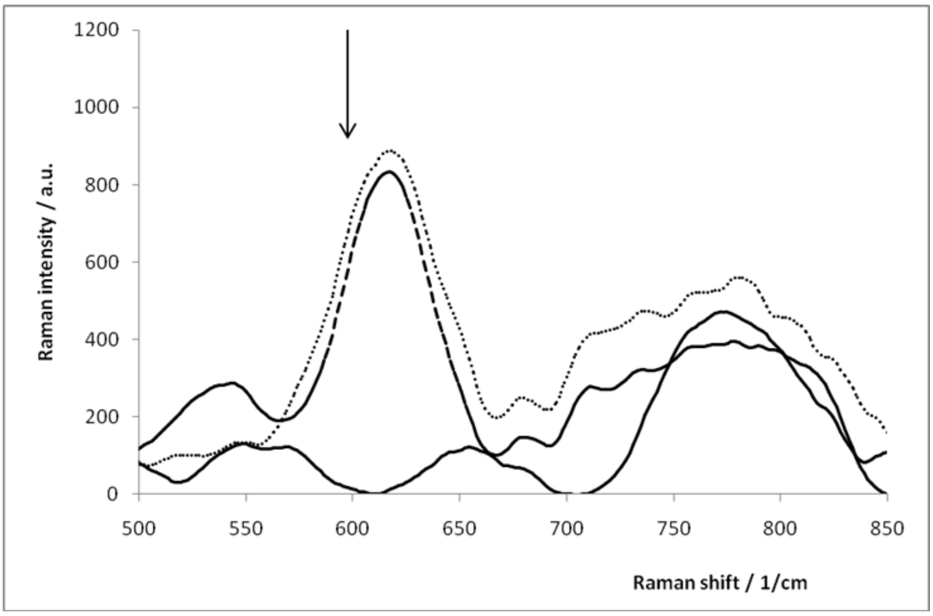


Figure 10. Extract from the Raman spectra of thymol blue (red), bromothymol blue (blue) and the electrochemically brominated thymol blue (blue, dashed)

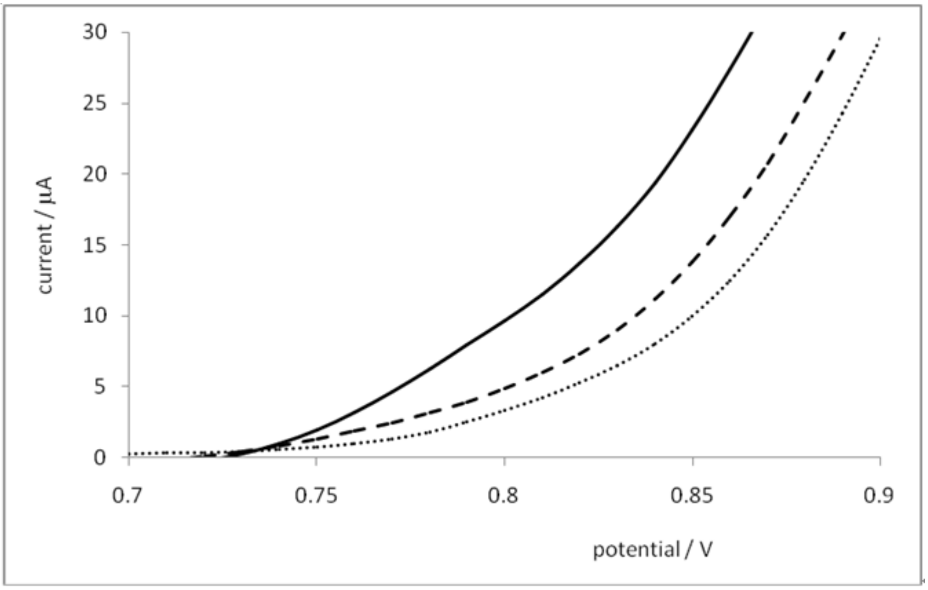


Figure 11. Linear-sweep voltammetry of phenol red / bromide for different working electrodes: solid line: C-CNT-SPE, dashed line: Au-SPE, dotted line: Pt-SPE

Figure 10 shows a section of the Raman spectra of thymol blue (solid line), bromothymol blue (dashed line) and the product of the electrosynthesis of thymol blue/bromide at 0.9 V (dotted line).

The correspondence between the Raman spectra of bromothymol blue and the reaction product of bromide and thymol blue during electrolysis at 0.9 V is clearly visible.

Schrader [11], Lambert et al [12] and Gullikson and Neilsen [13] report characteristic C-Br Raman bands at precisely this wavelength range. This proves that bromothymol blue is formed by the electro-organic reaction of thymol blue with bromine (by oxidation from bromide).

Phenol red shows similar behavior (see Supporting Information).

The question now arises as to whether the platinum electrode used acts as a catalyst during the bromination (here is a demonstration of the behaviour of phenol red for a change). In comparison to platinum, a gold and a carbon nanotube (C-CNT) SPE were used for the electro-organic synthesis and the reaction progress was measured by optical absorption.

The linear sweep voltammograms are shown in Figure 11. Irrespective of the electrodes used, the current flow starts at around 0.75 V and increases with approximately the same gradient (similar ohmic behaviour). The respective absorption of the resulting bromophenol blue (Figure 12) shows a very similar behaviour for the three electrodes used (λmax = 600 nm, maximum absorption ≈ 2000 units). We therefore assume that the bromination of phenol red is not a (platinum) catalysed reaction.

4. Decolouration after Prolonged Electrolysis

Figure 13 shows the absorption of thymol blue/bromide at different electrolysis times at 2 V. The spectrum has been zeroed at the beginning of the electrolysis to make the change in absorbance easier to see. The continuous curve is the absorption curve after 10 s, the dashed curve after 60 s electrolysis time. It can be seen that the bromothymol blue peak at around 600 nm decreases after a longer electrolysis time (arrow pointing downwards). At the same time, the peak at 500 nm and the IR peaks at 900 and 1100 nm increase. The concentration of thymol blue used was 0,1 mmol. Figure 13 shows that bromothymol blue was completely chemically transformed into more or less colourless products (see Supporting Information S7).

Changes can also be observed in the Raman spectra with longer electrolysis times. Figure 14 shows the comparison between bromothymol blue (solid line) and the electrolysis product after 60 s (dotted line). It is obvious that some Raman peaks decrease in intensity and others shift to longer wavenumbers (thick arrow). But there are also some new peaks (thin arrows).

Obviously, the C-Br vibrations are still present in the yellowish colourless product after 60 s of electrolysis. For C-Br stretching vibrations in aromatic compounds, the Raman shift typically occurs around 500–600 cm^{-1}.

The Raman shifts around 1600, 1050 and 800 cm^{-1} indicate a slight change in the aromatic vibrations. It can only be speculated which vibrations are involved in the newly formed vibrations around 670 and 1350 cm^{-1}. Lin-Vien et al [14] suggest ring deformation bands between 600 and 700 cm^{-1}, while substituent sensitive bands are found around 1300 cm^{-1}. Exact identification of the products is only possible with additional spectroscopic or chromatographic methods. However, to the best of the author's knowledge, no peak assignments can be found for either thymol blue or bromothymol blue.

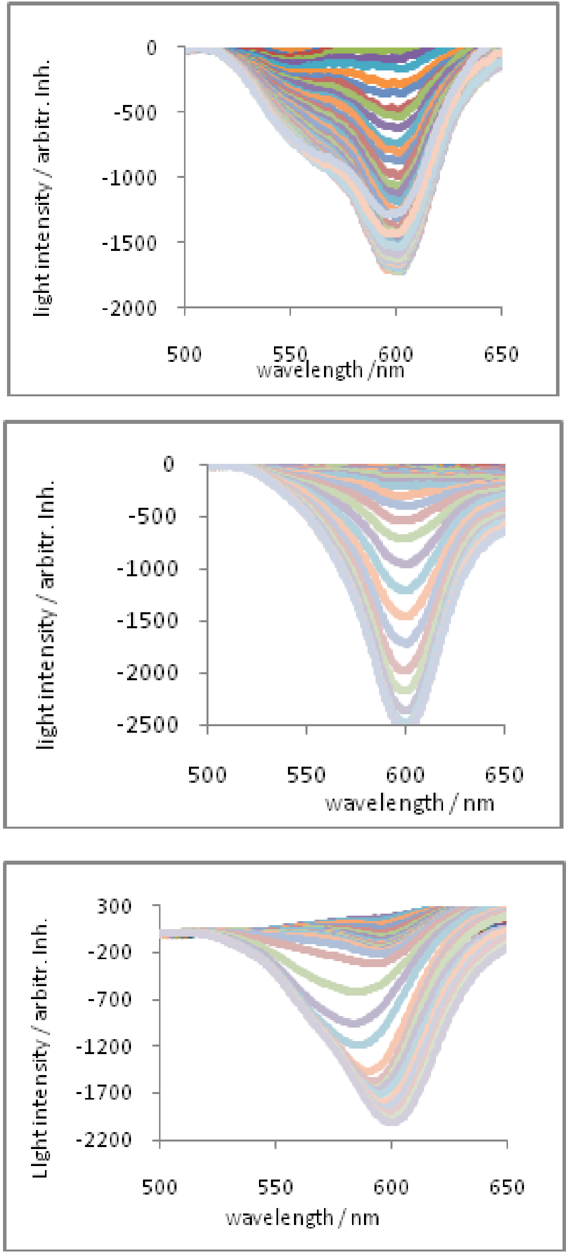


Figure 12. Change in the absorption of phenol red / bromide as a function of the applied potential between 0.7 V and 1 V for different working electrodes. Top: Pt, center: Au, bottomt: C-CNT

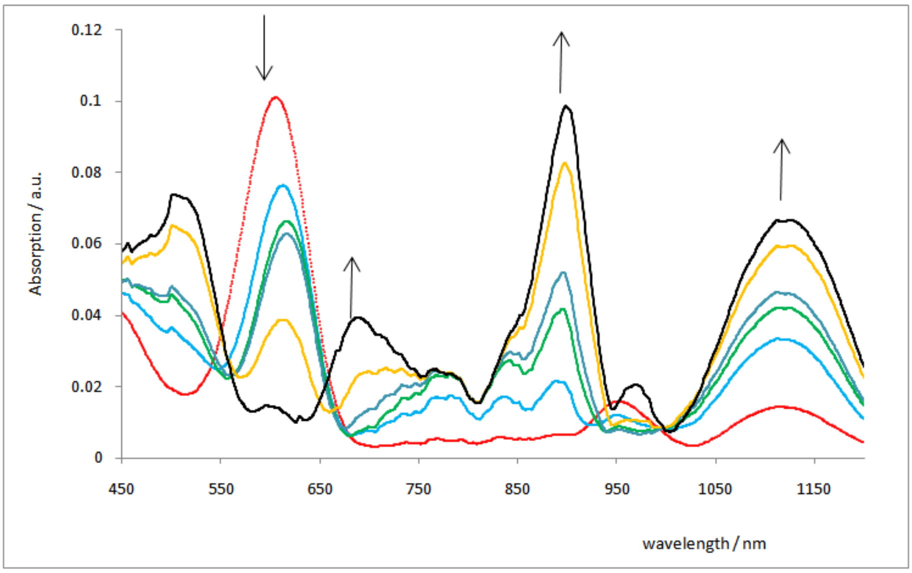


Figure 13. Absorption spectra after 10-60 s electrolysis of thymol blue at 2 V. Red dotted line after 10 s, black dashed line after 60 s. The other curves after 20, 30, 40 and 50 s. The arrows indicate the changes

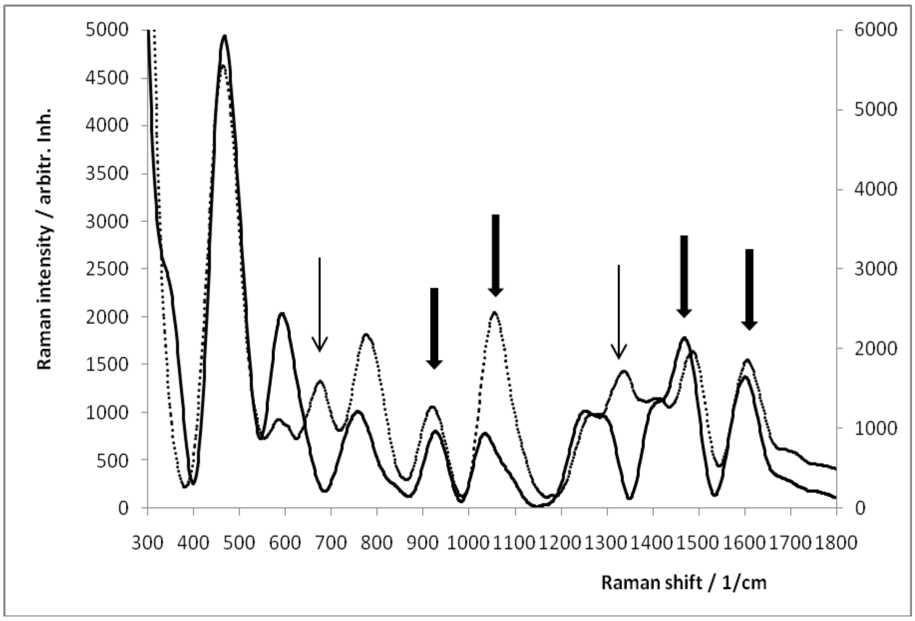


Figure 14. Solid line: Raman spectrum of bromothymol blue, dotted line: after 60 s electrolysis. Bold arrow: C-Br Raman vibration, thin arrow: newly formed Raman transitions

Summary

Absorpto- and Raman voltammetry were used to show that the bromination of blue (and phenol red) with bromine produced in situ by electrochemical oxidation leads to the products bromothymol blue (and bromophenol blue).

This confirms the measurements and conclusions of Ducci [4,5]. Electro-organic catalysis by platinum does not occur.

The identification of the colourless yellowish products after a longer electrolysis time requires further measurements.

References

[1] S.B. Beil, S.R. Waldvogel (2024). Trendbericht Organische Chemie 2023, Nachrichten aus der Chemie, 72, March, 47-49.

[2] J. Menig, H.J., Bader, H.J. Flintjer (1998). Unerwartete Reaktionswege bei der Kolbe-Elektrolyse Organische Elektrochemie im Chemieunterricht Chemkon 5/4, 174-180.

[3] P. Lanfermann, C. Weidmann, T. Schüler, T. Waitz (2021). Int. conference. New Perspectives in Science Education. *10th Conference Edition* (pp. 50-56). Filodiritto Publisher.

[4] M. Ducci (2024). Elektroorganische Synthesen: Bromierung von Thymolblau und Phenolrot, Chemkon 31/1, 15-21.

[5] M. Ducci (2023). Bromierung von Fluorescein – Elektrophile aromatische Substitution beim elektrochemischen Schreiben, Chemkon 30/4, 167-170.

[6] S. Schlücker (Ed.) (2011). Surface Enhanced Raman Spectroscopy, Analytical, Biophysical and Life Science Applications, Wiley-VCH, Weinheim.

[7] E. Smith, G. Dent (2019). Modern Raman Spectroscopy. A Practical Approach, Wiley, Hoboken.

[8] P.C. Lee, D. Meisel (1982). Adsorption and surface-enhanced Raman of dyes on silver and gold sols, J. Phys. Chem. 86, 3391-3395.

[9] M.T.F. Abedul, M. T. F. (2020). Laboratory Methods in Dynamic Electroanalysis, Elsevier, Amsterdam.

[10] D. Martin-Yerga, A. Perez-Junquera, M.B. Gonzalez-Garcia, J.V. Perales-Rondon, A. Heras, A. Colina, D. Hernandez-Santos, P. Fanjul-Bolado (2018). Quantitative Raman spectroelectrochemistry using silver screen-printed electrodesElectrochim. Acta, 264, 183-190.

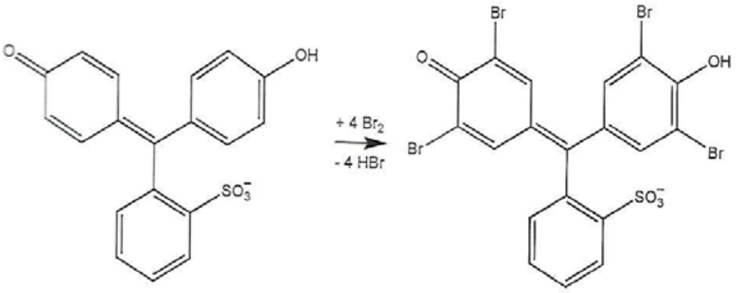
[11] B. Schrader (1989). Raman/Infrared Atlas of Organic Compound, VCH (2, Ed.), Weinheim.

[12] J.B. Lambert, S. Gronert, H.F. Shurvell, D.A. Lightner (2012), Spectroscopy. Structure elucidation in organic chemistry, Pearson, Munich.

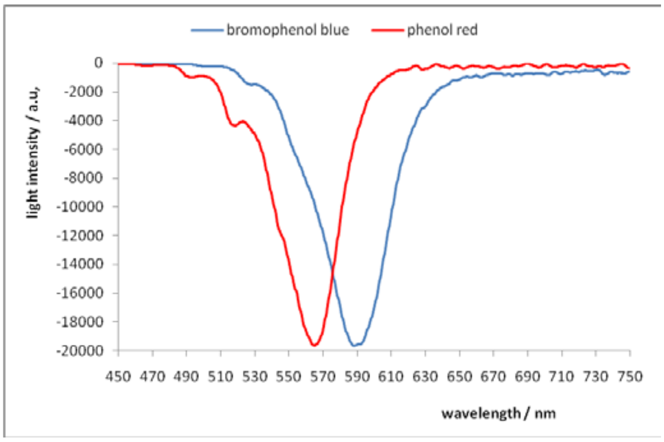
[13] C.W. Gullikson, J.R. Nielsen (1957). Vibrational spectra of gaseous vinyl chloride and vinyl bromide, J. Mol. Spectrosc. 1, 158–178.

[14] D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli (1991). The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules. Academic Press, Boston, p. 286.

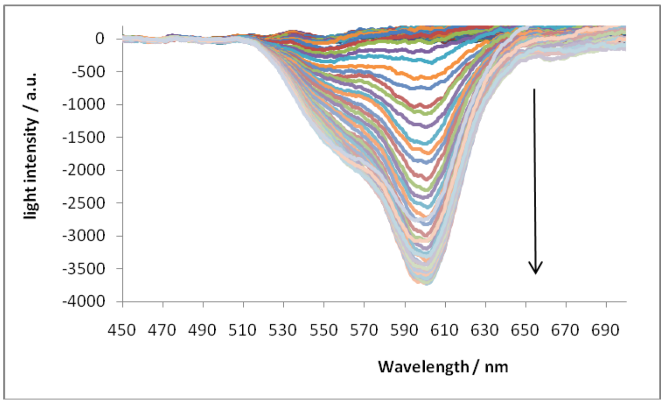
Supporting Infromation



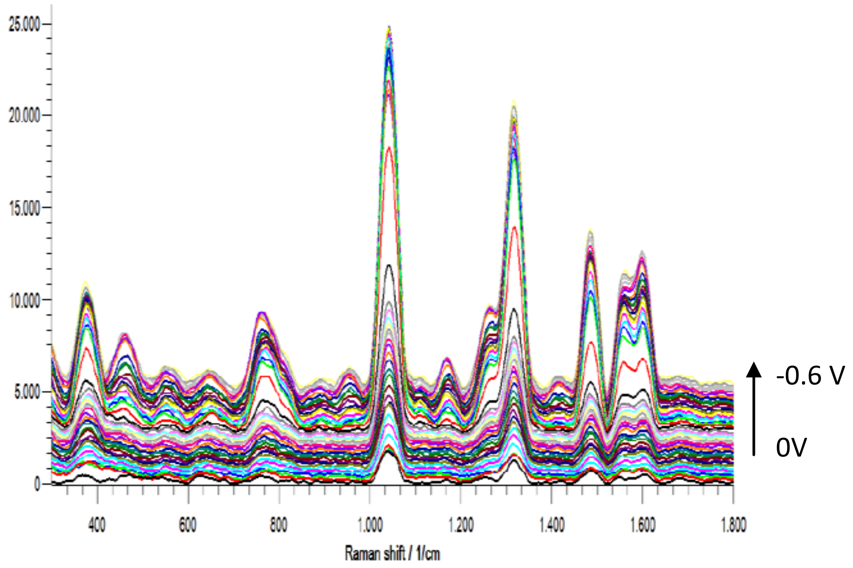
S1: Reaction scheme for the bromination of phenol red (left) to bromophenol blue (right)



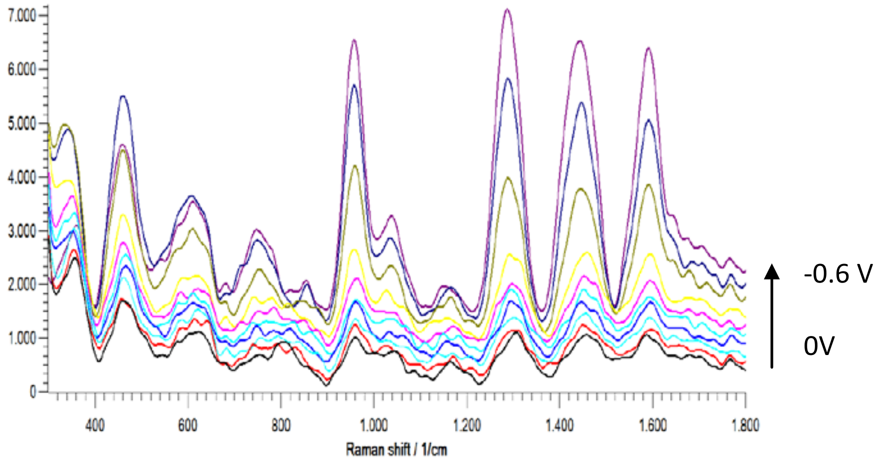
S2. Absorbance spectra at pH=6. Red line: phenol red, blue line: bromophenol blue.



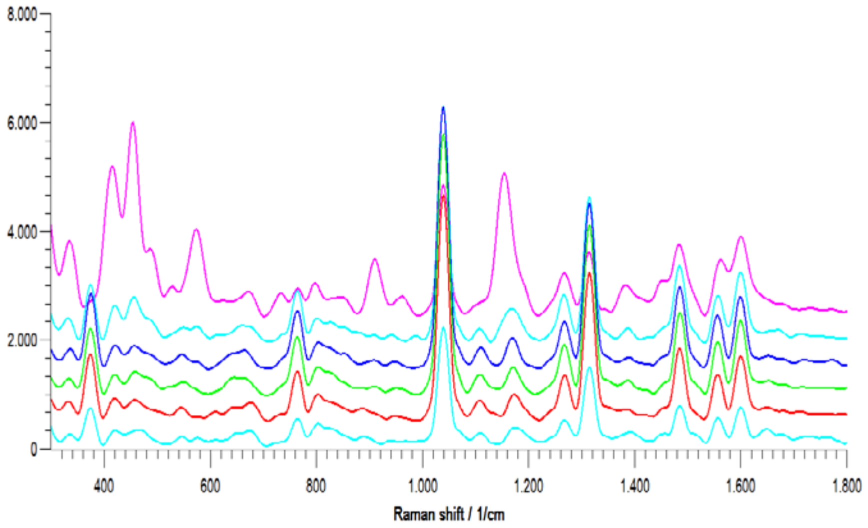
S3. Absorptovoltammogramm phenol red from 0 V to 1.5 V (arrow).



S4. Raman spectra of phenol red at different potentials from 0 V to -0.6 V.



S5. Raman spectrum of bromophenol blue at different potentials from 0 V to -0.6 V.



S6. SERS Raman spectra of phenol red between 0 and 1.5 V. Compare with S5. Peaks at 1300, 1500 and 1600 cm^{-1} increase/appear. This indicates the formation of bromophenol blue.

S7. Decolouration of a solution of thymol blue on a Pt electrode after 60 s of electrolysis at 2V.