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Iodimetric Determination of 2-Benzimidazolethiols and 2-Benzothiazolethiols

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In this paper a method of iodimetric determination of 2-benzimidazolethiol, 2-benzothiazolethiol and their derivatives in alkaline media is presented. In the volumetric titration with potentiometric end-point detection, the determination ranges are: 25–1000 μmol for 2-benzimidazolethiol (1a), 10–1000 μmol for 5-methoxy-2-benzimidazolethiol (1b), 10–1000 μmol for 5-nitro-2-benzimidazolethiol (1c), 25–1000 μmol for 2-benzothiazolethiol (2a) and 10–1000 μmol for 6-ethoxy-2-benzothiazolethiol (2b). In the coulometric determination with biamperometric end-point detection, 1–10 μmol of 1a and 0.25–40 μmol of 2a were successfully determined. Errors and relative standard deviations for all determinations were below 1%. For the compound 2a at higher concentration of sodium hydroxide potentiometric titration curve was unusually shaped. An addition of iodine resulted in a significant potential drop. The system examined does not reveal Nernstian behaviour.

Opisano metodę jodometrycznego oznaczania 2-benzimidazolotiolu, 2-benzotiazolotiolu i ich pochodnych w środowiskach zasadowych. Zakresy oznaczalności wynoszą: 25–1000 μmol dla 2-benzimidiazololtiolu (1a), 10–1000 μmol dla 5-metoksy-2-benzimidazolotiolu (1b), 10–1000 μmol dla 5-nitro-2-benzimidazolotiolu (1c), 25–1000 μmol dla 2-benzotiazolotiolu (2a) i 10–1000 μmol dla 6-etoksy-2-benzotiazolotiolu (2b) przy zastosowaniu techniki miareczkowania objętościowego z potencjometryczną detekcją punktu końcowego. W oznaczeniu kulometrycznym z biamperometryczną detekcją punktu końcowego oznaczono 1–10 μmol 1a i 0.25–40 μmol 2a. Błąd i względne odchylenie standardowe wszystkich oznaczeń nie przekraczały 1%. W roztworach bardziej stężonego NaOH uzyskano nietypowy przebieg krzywej miareczkowania dla związku 2a. Dodatek jodu powodował duży spadek potencjału. Badany układ nie zachowuje się zgodnie z równaniem Nernsta.

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Thiols have wide applications in industry and technology. They are used as corrosion inhibitors, accelerators and activators for rubber vulcanization and regeneration. The studied compounds are used in the production of photographic emulsions, developers and lithographic plate materials, as well as herbicides and pesticides. 2-Benzothiazolethiol (2a) is used as a collector in flotation of ores. 2-Benzimidazolethiol (1a) is used in production of cephalosporin and penicillin antibiotics.

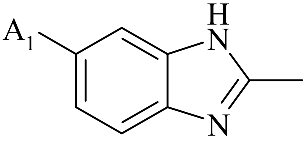
Titrimetric determination of 2-benzothiazolethiol (2a) with visual end-point detection using mercury(II) [1–3], silver(I) [1], cupric(II) [4-6], cerium(IV) [7], thallium(III) [8], chloramine T [9], chloramine B [9], iodine [10], nitric(V) acid [11] and sodium methanolate [12] as titrants has been widely reported. A acid-base titration of this compound has been also proposed [1]. Potentiometric titrations of 1a and 2a with silver(I) [13,14], zinc(II) [15], cupric(II) [16] have been also developed. 2-Benzimidazolethiol (1a) has been determined by the visual titration with iodine [17] and sodium methanolate [12]. 5-Nitro-2-benzimidazolethiol (1c) has been determined using hydrogen peroxide [18]. Determination of 1a and 2a has been also carried out using coulometric [19,20], biamperometric [21] and conductometric [22,23] methods.

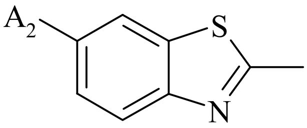
In this paper 2-benzimidazolethiol (1a), 2-benzothiazolethiol (2a) and their derivatives by their direct titration with iodine in alkaline medium were determined. The reaction scheme between iodine and thiols is given below:

$$\text{R-S}^- + 2\text{I}_2 + 4\text{OH}^- \longrightarrow \text{R-SO}_2^- + 4\text{I}^- + 2\text{H}_2\text{O} \qquad (1)$$

where:

R=





A_1: –H (1a), $-OCH_3$ (1b), $-NO_2$ (1c); A_2: –H (2a), $-OC_2H_5$ (2b)

Larger amounts of 2-benzimidazolethiols and 2-benzothiazolethiols were titrated volumetrically with potentiometric end-point detection. For smaller amounts of 2-benzimidazolethiol (1a) and 2-benzothiazolethiol (2a) coulometric titration with biamperometric end-point detection was carried out.

EXPERIMENTAL

Reagents and apparatus

KI, NaOH and I_2 were purchased from POCH, Gliwice, Poland. 2-Benzimidazolethiol (1a), 5-methoxy-2-benzimidazolethiol (1b), 5-nitro-2-benzimidazolethiol (1c) and 2-benzothiazolethiol (2a) from Aldrich Co., and 6-ethoxy-2-benzothiazolethiol (2b) from Lancaster were used. The studied thiols were purified by dissolving them in 2 mol L^{-1} NaOH solution, precipitating with glacial acetic acid and washing the precipitates with large amounts of water. Doubly distilled H_2O was used throughout. Standard solutions of iodine of the concentration of 0.01, 0.025, 0.05, 0.1 and 0.2 mol L^{-1} in KI solution were prepared. Stock solutions of thiols were obtained by dissolving weighed amount of the particular reagent in NaOH solution (Tab. 1).

Table 1. The results of potentiometric determination of the studied compounds in alkaline medium; n = 6

Compound	NaOH concentration mol L^{-1}	Taken μ mol	Found $\bar{x} \pm t_{0.95}\frac{s}{\sqrt{n}}$ μ mol
2-benzimidazolethiol (1a)	1	25.00	25.06 ± 0.06
		50.00	50.09 ± 0.08
		125.0	124.9 ± 0.3
		250.0	249.8 ± 0.5
		500.0	499.5 ± 1.1
		1000	1000 ± 1
5-methoxy-2-benzimidazolethiol (1b)	1	10.00	10.07 ± 0.03
		25.00	25.07 ± 0.07
		50.00	50.32 ± 0.05
		100.0	100.3 ± 0.2
		200.0	201.0 ± 0.4
		500.0	502.8 ± 0.5
		1000	1007 ± 2
5-nitro-2-benzimidazolethiol (1c)	1	10.00	10.07 ± 0.03
		25.00	25.07 ± 0.07
		50.00	49.70 ± 0.07
		100.0	99.18 ± 0.1
		200.0	198.5 ± 0.3
		500.0	496.8 ± 0.7
		1000	990.8 ± 1.3
2-benzothiazolethiol (2a)	0.1	25.00	24.94 ± 0.05
		50.00	49.95 ± 0.11
		125.0	124.8 ± 0.3
		250.0	249.5 ± 0.6
		500.0	498.9 ± 0.6
	0.5	1000	1007 ± 2

(Continuation on the next page)

Table 1. (Continuation)

6-ethoxy-2-benzothiazolethiol (2b)	1	10.00	10.08 ± 0.02
		25.00	25.13 ± 0.11
		50.00	50.30 ± 0.11
		100.0	100.6 ± 0.2
		200.0	200.7 ± 0.7
	2	500.0	502.1 ± 1.1
		1000	995.4 ± 2.2

A universal coulometric analyser (Radelkis, Budapest, Hungary), type OH-404 was applied to coulometric titrations,. An electrolysis cell [24] comprised two platinum electrodes of 5 cm^2 each, working electrode in a generating circuit and an OH–9381 double electrode in a biamperometric circuit. The solutions were mechanically stirred. The pH-meter, type CP–315 (Elmetron, Poland) with platinum and saturated calomel electrodes was used.

Procedures

Potentiometric titration. The samples of the compounds were dissolved in 50 mL of NaOH solution of an appropriate concentration (Tab. 1) and titrated with iodine using potentiometric end-point detection with a platinum indicator electrode and a saturated calomel reference electrode. The equivalence point was estimated from the inflection point on the curve. The initial amount of the analyte was calculated using the equation:

$$n = \frac{c(I) \times V}{z} \times 10^3$$

where: n – amount of the analyte [µmol]; c(*I*) – titrant concentration [mol·L^{-1}]; V – titrant volume at the end-point [mL]; z – number of electrons transferred in the single reaction, z = 4.

Coulometric titration. Coulometric titration was carried out in the solution given in Table 2. A sample solution was added to 20 mL of the reaction solution in the anodic compartment of the electrolysis cell. The cathodic compartment of the electrolysis cell was filled up with the same solution. The polarisation voltage applied was equal to 150 mV. Stabilising current was passed through the solution after starting the mechanical stirrer. The current magnitude in generating circuit (Tab. 2) depended on the amount of the analyte and was adjusted appropriately to maintain the titration time at the level of several minutes. Charge (Q) was measured after completing the titration of thiol since indicator current of 0.04 µA was obtained.

The content (µ mol) of the analyte in the tested sample was calculated according to Faraday's low:

$$n = \frac{\Delta Q}{zF} \times 10^3$$

where: DQ = Q – Q_0 (mC); Q_0 – blank titration charge; z – number of electrons transferred in the single reaction (z = 4); F – Faraday's constant (96 485 C·mol^{-1}).

Table 2. The results of coulometric titration of the studied compounds; n = 6

Compound	Reaction solution	Taken µ mol	Found $\bar{x} \pm t_{0.95} \frac{s}{\sqrt{n}}$ µ mol	Current mA
2-benzimidazolethiol (1a)	c(*KI*) = 1 mol L^{-1} c(*NaOH*) = 1 mol L^{-1}	1.000	1.003 ± 0.004	2.0
		2.000	1.994 ± 0.015	3.0
		5.000	4.992 ± 0.017	5.0
		10.00	9.979 ± 0.047	8.0
2-benzothiazolethiol (2a)	c(*KI*) = 1 mol L^{-1} c(*NaOH*) = 0.1 mol L^{-1}	0.2500	0.2525 ± 0.0029	0.5
		0.5000	0.5009 ± 0.0014	1.0
		1.000	1.000 ± 0.003	2.0
		2.000	1.999 ± 0.006	3.0
		5.000	4.989 ± 0.007	5.0
		10.00	9.996 ± 0.002	15
		20.00	19.97 ± 0.01	30
		40.00	39.77 ± 0.03	40

In the order to calculate the electric charge Q_0, which varied within the range 3–21 mC, a suitable amount of water instead of thiol was introduced into the reaction solution in the anodic compartment of the electrolysis cell.

RESULTS AND DISCUSSION

The results of iodimetric determination of 2-benzimidazolethiols and 2-benzothiazolethiols are presented in Tables 1–2. When larger or smaller amounts of the studied compounds were titrated, the error increased above 1%. Exemplary potentiometric titration curves of 2-benzothiazolethiol (2a) are shown in Figure 1.

In alkaline medium iodine reacts rapidly with thiols and after successive additions of iodine potential stabilises itself within 5–10 s.

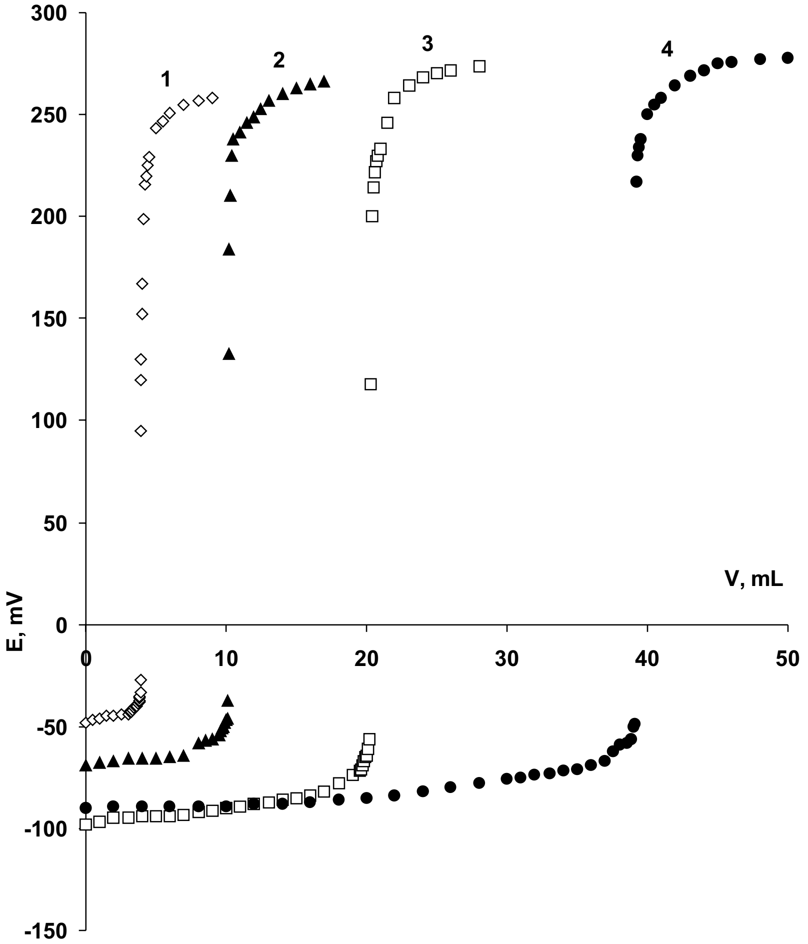


Figure 1. Potentiometric titration curves for: (1.) 50 μmol, (2.) 125 μmol, (3.) 250 μmol, (4.) 500 μmol of 2-benzothiazolethiol (2a) with 0.05 mol L^{-1} iodine in 0.1 mol L^{-1} NaOH solution

In neutral and acidic media, reaction of iodine with thiols is slower than in alkaline one. Moreover, in neutral medium potential drop on the titration curve is smaller than the one observed in alkaline medium (Fig. 2).

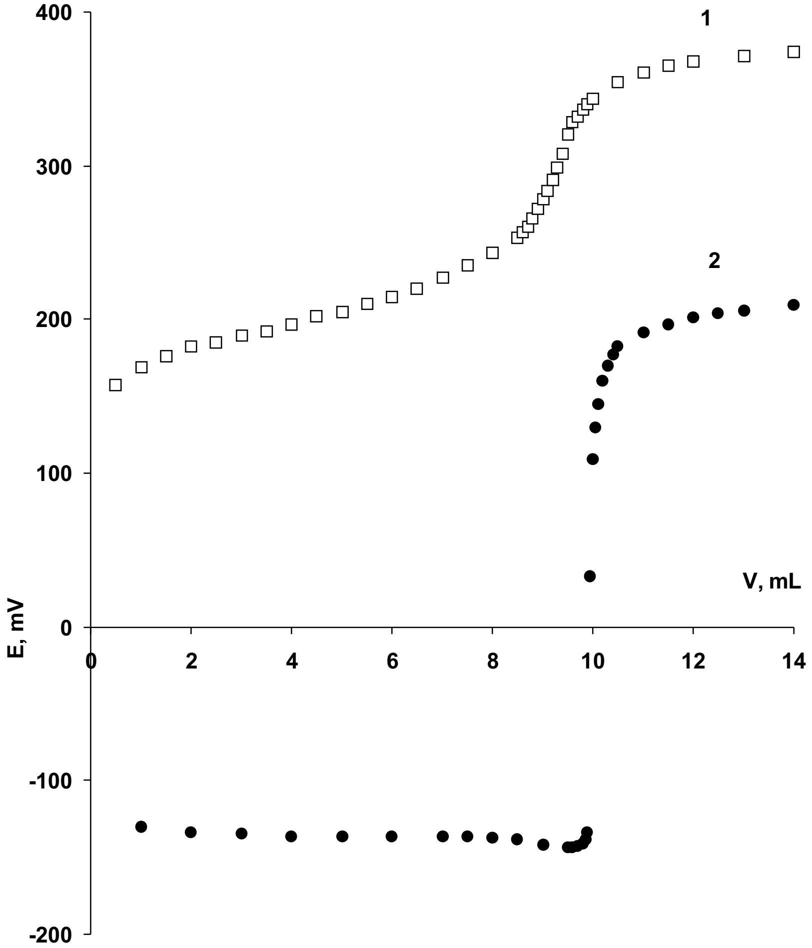


Figure 2. Potentiometric titration curves for: (1) 100 μmol of 2-benzimidazolethiol (1a) with 0.01 mol L^{-1} iodine in a neutral medium, (2) 125 μmol of 1a with 0.05 mol L^{-1} iodine in 1 mol L^{-1} NaOH solution

It is well known that iodine disproportionates quickly in alkaline medium to give iodide and oxoiodate(I) ions, and oxoiodate(I) becomes the oxidising agent. Titration in alkaline medium is possible if the reaction rate of oxoiodate(I) ions with thiol is higher than the rate of disproportionation of oxoiodate(I). It was found that the number of electrons transferred in the reaction of 2-benzimidazolethiols with iodine does not depend on the concentrations of NaOH in the solution in the range 0.5–10 mol L^{-1}, and is equal to 4. However, the number of electrons transferred in the reaction of iodine with 2-benzothiazolethiol (2a) depends on the concentration of NaOH. An increase of its concentration over 1 mol L^{-1} resulted in the increase of the number of electrons transferred in the reaction, since the product of reaction (1) reacted further itself with iodine according to Equation 2:

$$\text{R-SO}_2^- + 2\text{I}_2 + 6\text{OH}^- \longrightarrow \text{RO}^- + 4\text{I}^- + \text{SO}_4^{2-} + 3\text{H}_2\text{O} \qquad (2)$$

Concentration of NaOH was appropriately chosen depending on the concentration range of the titrated thiols in order to provide the reaction scheme according to Equation 1. Titration of 25–500 μmol of 2-benzothiazolethiol (2a) required the initial NaOH concentration to be 0.1 mol L^{-1}. Yet, titration of 1000 μmol of this compound requires a higher initial concentration of NaOH (0.5 mol L^{-1}). Determination of 500–1000 μmol of 6-ethoxy-2-benzothiazolethiol (2b) required even higher concentration of NaOH (2 mol L^{-1}) than it was needed for the titration of 10–200 μmol of 2b.

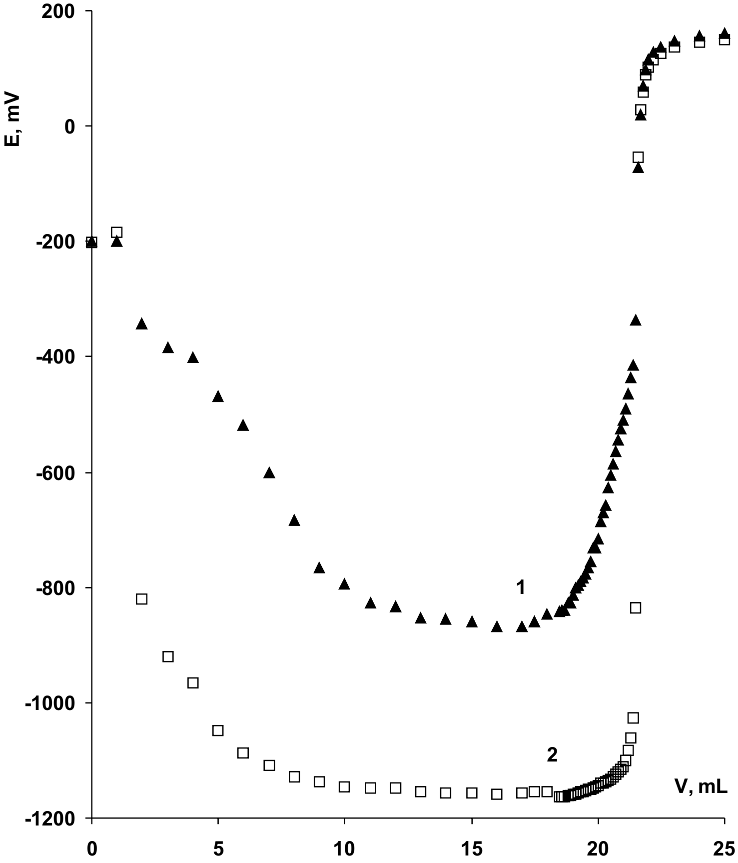


Figure 3. Potentiometric titration curves for 250 μmol of 2-benzothiazolethiol (2a) with 0.1 mol L^{-1} iodine in 5 mol L^{-1} NaOH solution using: (1) gold indicator electrode, (2) platinum indicator electrode

The shape of potentiometric titration curve of 2-benzothiazolethiol (2a) at higher concentration of NaOH is noteworthy and depends on the type of the indicator electrode (platinum, gold) (Fig. 3). An addition of iodine results in a strong potential drop. Similar behaviour was observed during titration of pyrimidine-2-thiol [25], thiopental [26], 2-thiocytosine [27], 1-phenyl-1*H*-tetrazole-5-thiol [28] and 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol [28]. This phenomenon occurs at platinum and gold electrodes, and is a result of adsorption and charging of the double electric layer at the phase boundary. It was not observed during titration of 2-benzimidazolethiol (1a).

Potentiometric end-point detection in coulometric titration of small amounts of 2-benzimidazolethiol (1a) and 2-benzothiazolethiol (2a) is impossible, owing to the slow response of the platinum indicator electrode at low concentration of the analyte. One can overcome this obstacle and correct the coulometric results by applying the biamperometric indicator system for the determination of (1a) and (2a).

The results of coulometric determination of (1a) and (2a) in alkaline medium were satisfactory in the presence of 1 mol L^{-1} NaOH and 1 mol L^{-1} KI, and 0.1 mol L^{-1} NaOH and 1 mol L^{-1} KI, respectively. Under these conditions the reaction between thiol and iodine proceeds stoichiometrically and the number of electrons transferred in the reaction of oxidised compound is exactly 4. The reaction solution used ensured 100% current efficiency [29]. Moreover, alkaline medium provides stability of iodide ions in the presence of oxygen.

It was found that 2-benzothiazolethiol (2a) requires a lower concentration of sodium hydroxide during titration than 2-benzimidazolethiol (1a). In the molecule of (2a) the second nitrogen atom is replaced with sulfur, and electron density of the sulfur atom in –SH group is smaller than that in (1a). As a result (2a) undergoes oxidation easier than (1a). Methoxy- and nitro- groups do not influence the rate of reaction (1) in comparison with (1a).

For the compounds existing in the thione form only, the potentiometric titration with iodine in an alkaline medium does not give satisfactory results, since the reaction rate between thione and iodine is too slow. Iodine reacts fast enough only with a thiol form. The potentiometric titration of 3-methylbenzothiazole-2-thione with iodine is unfeasible, whereas that of 2-benzothiazolethiol (2a) can be carried out successfully.

In comparison to the methods previously reported [1–23] iodimetric determination of 2-benzimidazolethiols and 2-benzothiazolethiols provides short analysis time, high precision and accuracy, the possibility of determination over a broader range of concentrations, simplicity and the use of commonly available reagents. The coulometric method worked out is partly automated and, as an absolute one, requires no standard solutions.

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