Chem. Anal. (Warsaw), **48**, 939 (2003)

Unusual Potentiometric Titration Curves of 2,8-Dimercapto-6-hydroxypurine and 4,4-Dimethyloxazolidine-2-thione with Iodine

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Key words: 2,8-dimercapto-6-hydroxypurine, 4,4-dimethyloxazolidine-2-thione, potentiometric titration, iodimetric determination

Iodimetric volumetric titration with potentiometric detection of the end-point has been performed in order to determine 2,8-dimercapto-6-hydroxypurine and 4,4-dimethyloxazolidine-2-thione in strongly alkaline medium. Determination range found was 100-500 μmol for 2,8-dimercapto-6-hydroxypurine and 50-1000 μmol for 4,4-dimethyloxazolidine-2-thione. The errors and the relative standard deviations were below 1 %. The shapes of the obtained potentiometric titration curves depended on the concentrations of sodium hydroxide and the analytes, the material of the working electrode (platinum, gold) and its surface. Addition of iodine resulted in a significant potential drop. The studied systems did not exhibit Nernstian behaviour.

Przeprowadzono jodometryczne miareczkowanie 2,8-dimerkapto-6-hydroksypuryny i 4,4-dimetylooksazolidyno-2-tionu w silnie zasadowym środowisku z potencjometryczną detekcją punktu końcowego. Zakresy oznaczalności dla badanych analitów wyniosły odpowiednio: 100–500 μmoli i 50–1000 μmoli. Błąd i względne odchylenie standardowe wszystkich oznaczeń nie przekraczało 1%. Stwierdzono nietypowy kształt krzywych miareczkowania potencjometrycznego i jego zależność od stężenia wodorotlenku sodu i analitów, rodzaju elektrody wskaźnikowej (platyna, złoto) i jej powierzchni. Wprowadzenie jodu powodowało znaczny spadek potencjału elektrody pracującej. Badane układy nie spełniają równania Nernsta.

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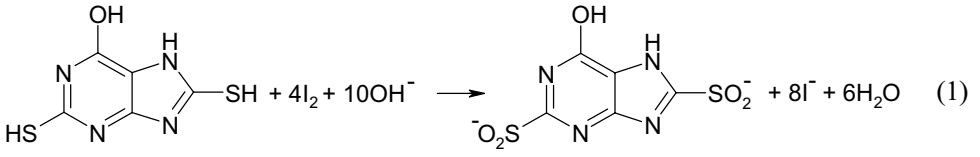
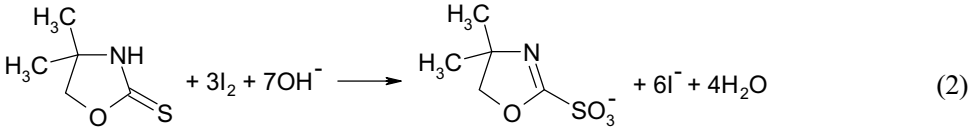
2,8-dimercapto-6-hydroxypurine and 4,4-dimethyloxazolidine-2-thione are known for their practical applications. 2,8-dimercapto-6-hydroxypurine is used in the production of antiviral agents and immunostimulants [1,2], while 4,4-dimethyloxazolidine-2-thione serves as a defoliant and insecticide [3].

This paper presents the method of potentiometric determination of both these compounds by their direct titration with iodine in alkaline medium using platinum or gold indicator electrode. The respective reaction schemes and their stoichiometry are given below (Eqs. 1 and 2):



(1)



(2)

Previously we had reported a significant potential drop that occurred during the iodimetric titration of some thiols: 2-thiocytosine [4], 2-mercaptopirymidine [5] and 1-phenyl-1H-tetrazole-5-thiol [6]. This was observed at NaOH concentration higher than previously used by us. In this paper the applied NaOH concentration was so high that it led to the substantial potential drop, which was in contrast to the Nernst equation.

EXPERIMENTAL

Reagents and apparatus

All the reagents were of the analytical purity: sodium hydroxide, potassium iodide, iodine (Polskie Odczynniki Chemiczne), 2,8-dimercapto-6-hydroxypurine (98%, Lancaster Synthesis Ltd.) and 4,4-dimethyloxazolidine-2-thione (99%, Fluka). Doubly distilled water was used throughout. Iodine standard solutions: 0.03, 0.05, 0.1 and 0.15 mol L^{-1} were prepared. Stock solutions were obtained by dissolving an appropriate weighed amount of the respective compound in a suitable solution of sodium hydroxide. The pH meter, type CP–315, Elmetron with a saturated calomel electrode and platinum or gold electrode, was used. Indicator electrodes of variously shaped working surface (wire, plate) were used.

Procedure

Thiol samples were dissolved in 50 mL of a suitable sodium hydroxide solution (concentrations given in Table) and titrated with iodine. The end-point was detected potentiometrically in a circuit comprising platinum electrode as the indicator, and saturated calomel electrode as the reference. 5 s waiting time was applied after each addition of iodine to let the potential response stabilise. The equivalence point of the reaction was determined from the first derivative curve. Close to the end-point of the titration a small amount of iodine (0.02–0.05 mL) was introduced.

RESULTS AND DISCUSSION

In acidic and neutral media thiols react very slow with iodine, and thus iodimetric titration is impossible. However, in alkaline media the stoichiometry of the reactions is different. Iodine disproportionates quickly in alkaline medium to give iodide and iodate(I) ions, the latter being the virtual oxidising agent. The titration in alkaline medium is only possible if the reaction of iodate(I) ions with thiol is faster than the disproportionation of iodate(I) ions.

It has been found that the number of electrons transferred in the reaction of 1 mol of the studied thiol with iodine depends on the concentration of sodium hydroxide in the solution. Too low concentration of sodium hydroxide prevents the reaction from proceeding stoichiometrically. In consequence, the number of electrons transferred per 1 mol of the compound is lower than 8 for 2,8-dimercapto-6-hydroxypurine, and than 6 for 4,4-dimethyloxazolidine-2-thione. In the case of 4,4-dimethyloxazolidine-2-thione an increase of sodium hydroxide concentration over 4 mol L^{-1} was followed by an increase of the number of electrons transferred, since the product of reaction (2) reacts further with iodine according to the Eq.3:

$$R\text{-}SO_3^- + I_2 + 2OH^- \longrightarrow RO^- + 2I^- + SO_4^{2-} + H_2O \qquad (3)$$

However, for 2,8-dimercapto-6-hydroxypurine an increase of sodium hydroxide concentration over 7 mol L^{-1} does not change the number of electrons transferred.

Potentiometric titration curves of 4,4-dimethyloxazolidine-2-thione and 2,8-dimercapto-6-hydroxypurine were uniquely shaped at higher concentrations of sodium hydroxide (Figs. 1–3). A small addition of iodine resulted in a significant potential drop in the initial part of the curve, which did not occur at lower concentration of sodium hydroxide. The more one increased the concentration of sodium hydroxide, the smaller volume of iodine was sufficient to observe the potential drop (Fig. 1, curves b, c). The same phenomenon was observed when 2,8-dimercapto-6-hydroxypurine and 2-mercaptopyrimidine [5] were titrated.

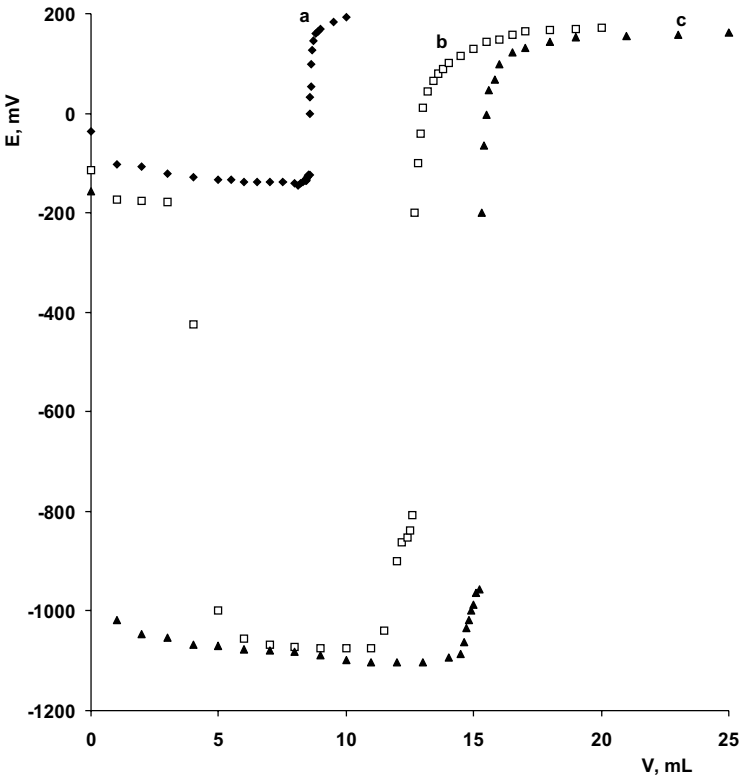


Figure 1. Potentiometric titration curves of 100 μmol of 4,4-dimethyloxazolidine-2-thione with 0.05 mol L^{-1} iodine in: a) 1 mol L^{-1}, b) 5 mol L^{-1}, c) 10 mol L^{-1} sodium hydroxide solution. Indicator electrode: platinum wire

It has been found that the shape of potentiometric titration curves depended on the concentration of the analytes. If one titrated 50–200 μmol of 4,4-dimethyloxazolidine-2-thione in 4 mol L^{-1} NaOH the shapes of the titration curves were typical and not distorted by the potential drop. (Fig. 2, curve a). However, if larger amounts of this analyte were present in the sample, the potential drop was observed (Fig. 2, curve b and c). In the case of 2,8-dimercapto-6-hydroxypurine the potential drop appeared for the analyte content of 100–500 μmol (Fig. 3). When 100 μmol of 2,8-dimercapto-6-hydroxypurine (Fig. 3, curve a) or 500 μmol of 4,4-dimethyloxazolidine-2-thione (Fig. 2, curve b) were titrated the potential drop occurred after almost the whole required (according to the stoichiometry) amount of iodine added was already consumed. When larger amounts (500 μmol of 2,8-dimercapto-6-hydroxypurine (Fig. 3, curve b) or 1000 μmol of 4,4-dimethyloxazolidine-2-thione (Fig. 2, curve c)) were titrated, the potential drop appeared at the beginning of titration.

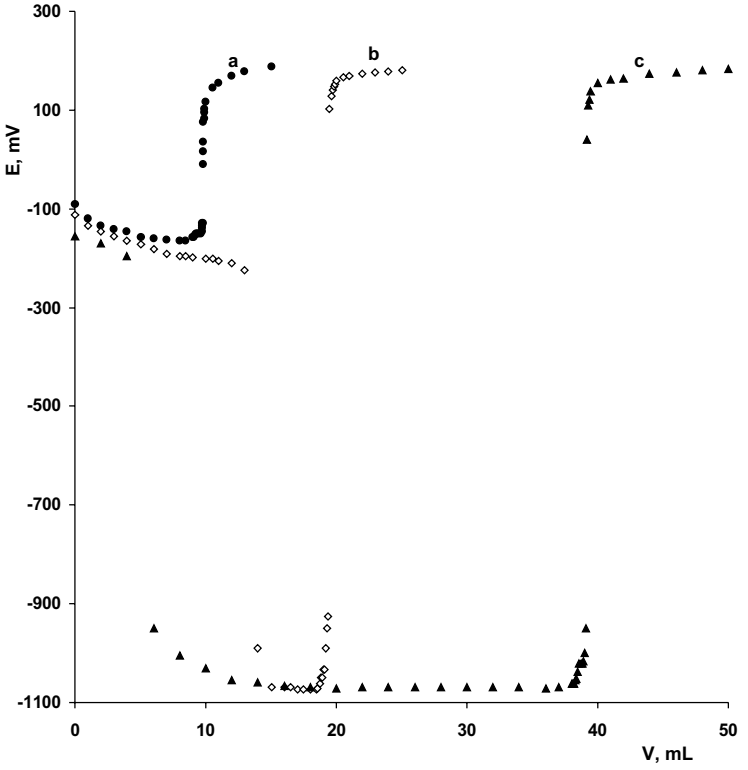


Figure 2. Potentiometric titration curves of: a) 50 μmol of 4,4-dimethyloxazolidine-2-thione with 0.03 mol L^{-1}iodine, b) 500 μmol and c) 1000 μmol of 4,4-dimethyloxazolidine-2-thione with 0.15 mol L^{-1} iodine. Sodium hydroxide concentration: 4 mol L^{-1}. Indicator electrode: platinum wire

The proposed determination method leads to the significant potential increase at the equivalence point (800–1000 mV/0.1 mL of the titrant – Fig. 2, curves b, c; Fig. 3), which does not occur in other potentiometric titrations.

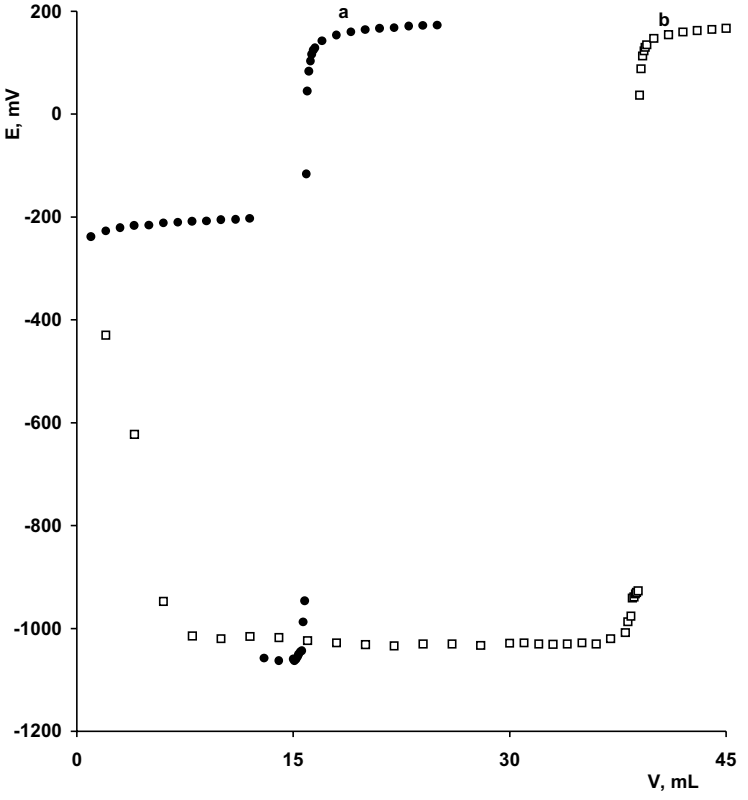


Figure 3. Potentiometric titration curves of: a) 100 μmol of 2,8-dimercapto-6-hydroxypurine with 0.05 mol L^{-1} iodine, b) 500 μmol of 2,8-dimercapto-6-hydroxypurine with 0.1 mol L^{-1} iodine. Sodium hydroxide concentration: 7 mol L^{-1}. Indicator electrode: platinum wire

In the case of potentiometric titration of 4,4-dimethyloxazolidine-2-thione the potential drop appeared when platinum or gold indicator electrode was used. Moreover, when a gold wire indicator electrode was used for the potentiometric titration of 2,8-dimercapto-6-hydroxypurine, the shape of the response was typical (Fig 4, curve a). With platinum indicator electrode (wire and plate) and gold plate electrode the potential drop affected initial parts of the curves (Fig. 4, curves b-d).

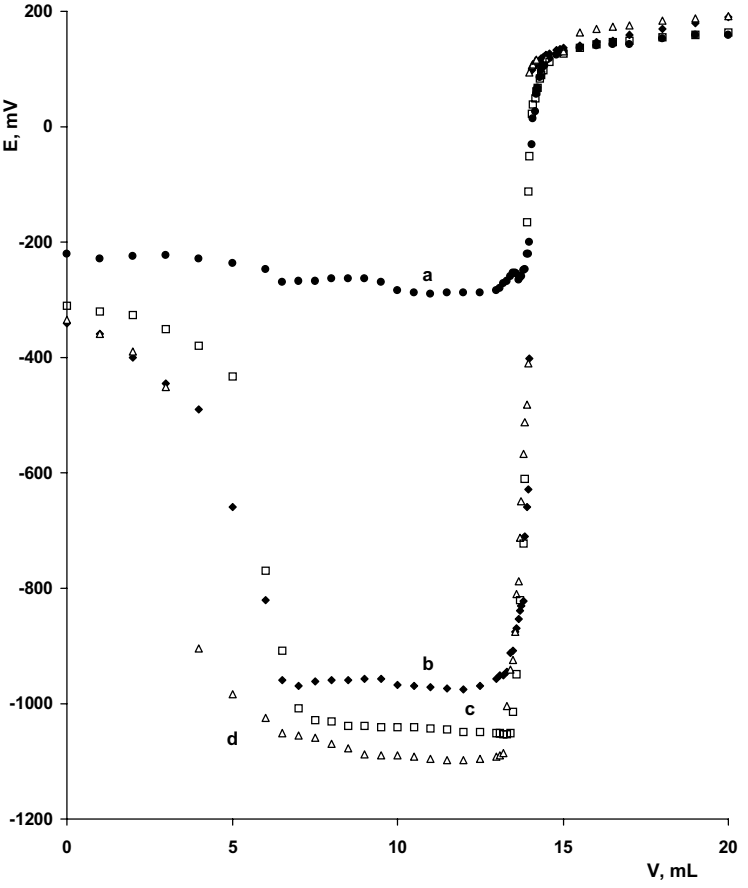


Figure 4. Potentiometric titration curves of 200 μmol of 2,8-dimercapto-6-hydroxypurine with 0.1 mol L^{-1} iodine in 7 mol L^{-1} sodium hydroxide using: a) gold wire, b) gold plate, c) platinum wire and d) platinum plate indicator electrode

In addition, our research indicates that the preparation procedure of the electrodes used is not indifferent to the shapes of the obtained curves. The metal used for the preparation of the given electrode has different structures depending on how it is shaped – as a wire or as a plate. In the first case the metal was drawn, in the second one it was rolled.

It has been found that the shapes of the titration curves obtained at high sodium hydroxide concentration depend on the material of the indicator electrode, and on the concentrations of sodium hydroxide and the analytes. This phenomenon is related to the adsorption processes and charging of the double layer, both occurring at the phase boundary of the indicator electrode.

The results of the determination in optimised conditions have been presented in Table 1.

Table 1. The results of the determination of thiols ($n = 6$)

Compound	Concentration of NaOH mol L^{-1}	Taken, μmol	Found, μmol $\bar{x} \pm t_{0.95} \frac{s}{\sqrt{n}}$	RSD, %
2,8-Dimercapto-6-hydroxypurine	7	100.0	100.0 ± 0.6	0.58
		200.0	199.7 ± 1.1	0.53
		500.0	496.8 ± 1.1	0.20
4,4-Dimethyl-oxazolidine-2-thione	4	50.00	50.12 ± 0.18	0.34
		100.0	100.3 ± 0.4	0.41
		200.0	199.6 ± 0.6	0.29
		500.0	501.4 ± 2.7	0.51
		1000	1008 ± 2	0.16

Acknowledgements

This work was supported by grants No 3 TO9A 117 16 from the State Committee of Scientific Research, Warsaw, Poland and No 505/260 from the University of Łódź.

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Received November 2002
Accepted June 2003