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POTENTIOMETRIC STUDIES ON THIOACETAMIDE BY MEANS OF A SULPHIDE ION-SELECTIVE MEMBRANE ELECTRODE

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Thioacetamide is a well known reagent which is used in both qualitative and quantitative analysis[1,2].

In the present report, a rapid and accurate potentiometric method is described for the determination of thioacetamide with a sulphide ion-selective membrane electrode. The products of the reaction with silver nitrate titrant have been identified.

EXPERIMENTAL

E.m.f. measurements were taken with a Radelkis Precision pH meter Type OP-205 (Radelkis, Budapest, Hungary). A Radelkis sulphide ion-selective electrode Type OP-S-711 and a Metrohm pH glass electrode were used as indicator electrodes and a saturated calomel electrode as reference electrode. The calomel electrode was connected with the solution to be titrated by a 1 *M* potassium nitrate–agar salt bridge.

Ultraviolet and visible spectra were recorded by a Unicam SP 700 spectrophotometer, and the infrared spectra by a Zeiss UR-10 instrument.

All reagents used were of analytical grade.

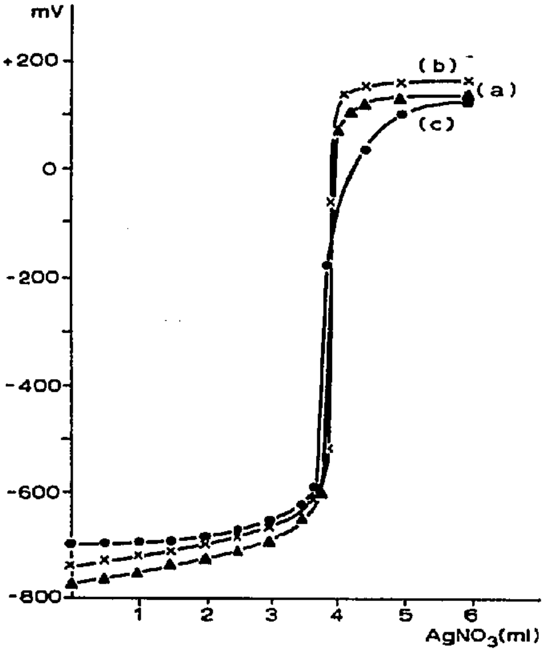
A thioacetamide stock solution (10^{-1} *M*) was prepared by weighing and dissolving the appropriate amount of the reagent.

Dilute standard solutions were prepared from the stock solution by serial dilution.

RESULTS

The potentiometric titration curves of 10^{-1}–10^{-3} *M* thioacetamide solutions were established in 1 *M* sodium hydroxide (Fig. 1), in 0.1 *M* sodium hydroxide (Fig. 2), in 0.01 *M* ammonia solution (Fig. 3), in pure distilled water (Fig. 4), and in 0.1 *M* acetic acid (Fig. 9). Silver nitrate solution of the equivalent concentration was used as titrant in every case.

In Figs. 5 and 6, the potential and pH change are shown for the titration of thioacetamide of the same concentration, in 0.01–0.05 *M* and 0.1 *M* sodium hydroxide. In Figs. 7 and 8 are presented the changes in the course of the titration of thioacetamide in 0.01–0.1 *M* ammonia solution.



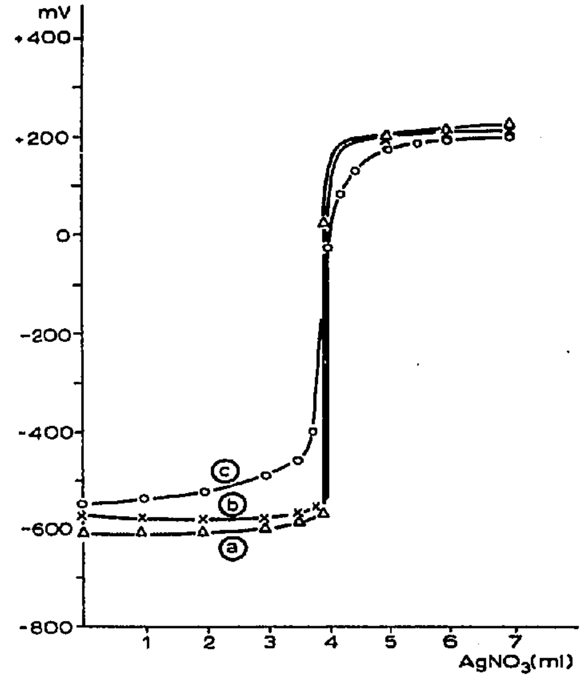


Fig. 1. Potentiometric titration curves of thioacetamide in 1 *M* sodium hydroxide. (a) 10^{-1} *M* thioacetamide; (b) 10^{-2} *M* thioacetamide; (c) 10^{-3} *M* thioacetamide.

Fig. 2. Potentiometric titration curves of thioacetamide in 10^{-1} *M* sodium hydroxide. (a, b, c) As in Fig. 1.

In Fig. 10 are shown the titration curves obtained in the presence of 0.1 *M* and 0.5 *M* nitric acid.

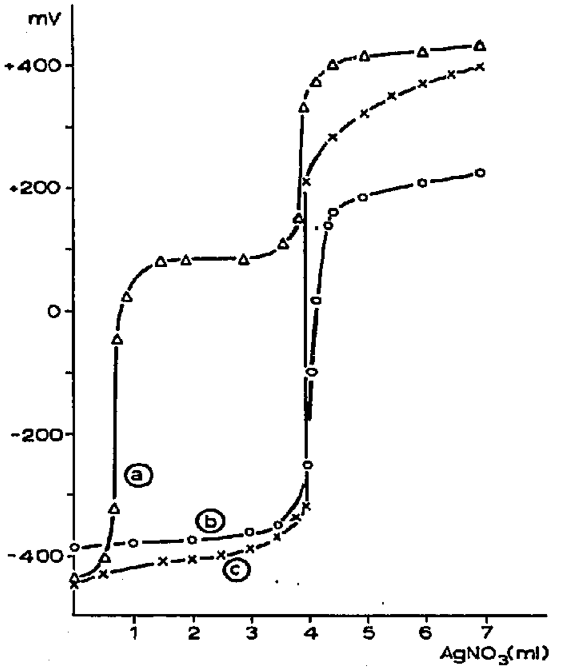
DISCUSSION

As may be seen in Figs. 1–4, thioacetamide can be titrated in the concentration range 10^{-1}–10^{-3} *M* in distilled water, or in the presence of 0.1 or 1 *M* sodium hydroxide or in 0.01 *M* ammonia solution with standard silver nitrate solution. The changes which occur during titration are sensitively followed by the sulphide ion-selective electrode. However, the titration of 10^{-4} *M* thioacetamide takes a long time in aqueous medium, as the setting up of the equilibrium potential at the electrode is slow at these low concentrations.

In most cases, one potential jump can be observed on the titration curves at a position corresponding to the stoichiometric reaction of thioacetamide with silver nitrate.

The titration curve obtained with 10^{-1} *M* thioacetamide at pH 12 is different, exhibiting two potential jumps, the second of which can be used for the determination of thioacetamide (Fig. 3).

In order to establish the reason for the first potential jump on curve "a" in Fig. 3, potential and pH measurements were made at constant thioacetamide and varying alkali concentrations (Figs. 5–8).



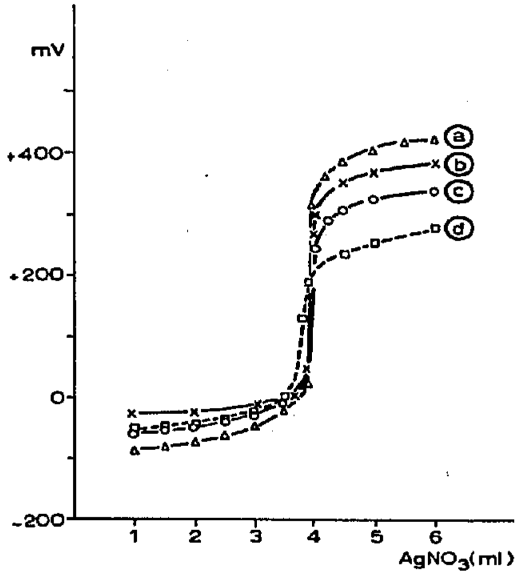


Fig. 3. Potentiometric titration curves of thioacetamide in 10^{-2} *M* ammonia. (a, b, c) As in Fig. 1.

Fig. 4. Potentiometric titration curves of thioacetamide in pure distilled water. (a) 10^{-1} *M* thioacetamide; (b) 10^{-2} *M* Thioacetamide; (c) 10^{-3} *M* thioacetamide; (d) 10^{-4} *M* thioacetamide.

A comparison of the sulphide electrode potential curves with the pH curves shows that the potential of the sulphide electrode changes suddenly at the same volume of standard solution added as a sudden pH change occurs. This is indicative of a remarkable change in sulphide concentration (first potential jumps in Figs. 5 and 7).

A stoichiometric reaction proceeds also in 0.1 *M* acetic acid. The equivalent weight of thioacetamide is equal to half its molecular weight in these titrations.

In the direct measurement of thioacetamide by means of the sulphide ion-selective electrode, a 30-mV change in electrode potential corresponds to a decade change in thioacetamide concentration in the range 10^{-1} to 10^{-3} *M*, in 0.1 *M* and 1 *M* sodium hydroxide. This also shows that the electrode measures the product of the hydrolysis.

In the presence of 0.1 *M* nitric acid the reaction proceeds in the same way as in alkaline medium or in pure distilled water, *i.e.*, one molecule of thioacetamide reacts with two molecules of silver nitrate. In 0.5 *M* or more concentrated nitric acid solutions, however, a different reaction takes place, and one mole of thioacetamide reacts with only one mole of silver nitrate. In this case the equivalent weight of thioacetamide is equal to its molecular weight.

IDENTIFICATION OF THE PRODUCTS OF TITRATION

In the titration of thioacetamide with silver nitrate in distilled water and in

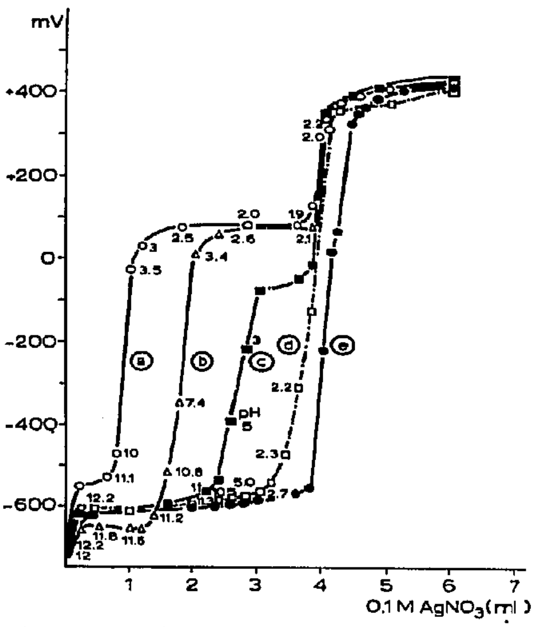


Fig. 5. Potentiometric titration curves of 10^{-1} *M* thioacetamide in the presence of sodium hydroxide. (a) 0.01 *M*; (b) 0.02 *M*; (c) 0.03 *M*; (d) 0.04 *M*; (e) 0.05 *M*; (f) 0.1 *M*.

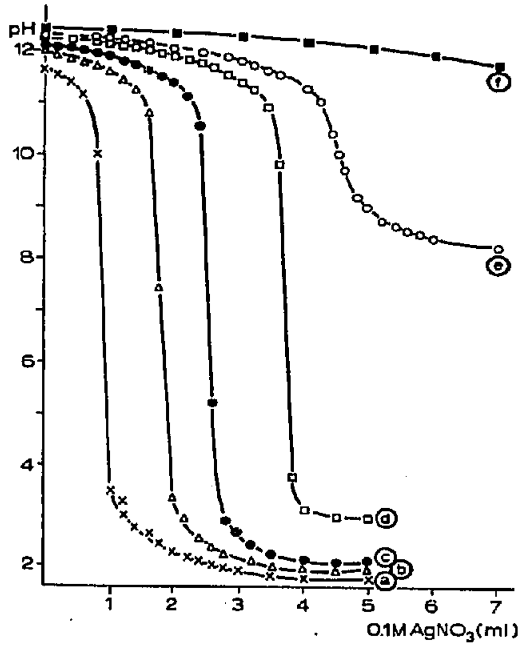


Fig. 6. pH titration curves of 10^{-1} *M* thioacetamide in the presence of sodium hydroxide. (a–f) As in Fig. 5.

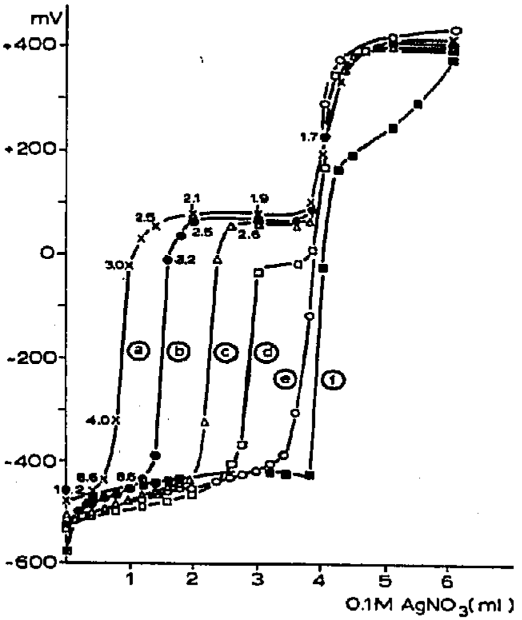


Fig. 7. Potentiometric titration curves of 10^{-1} *M* thioacetamide in ammonia solution. (a–f) As in Fig. 5.

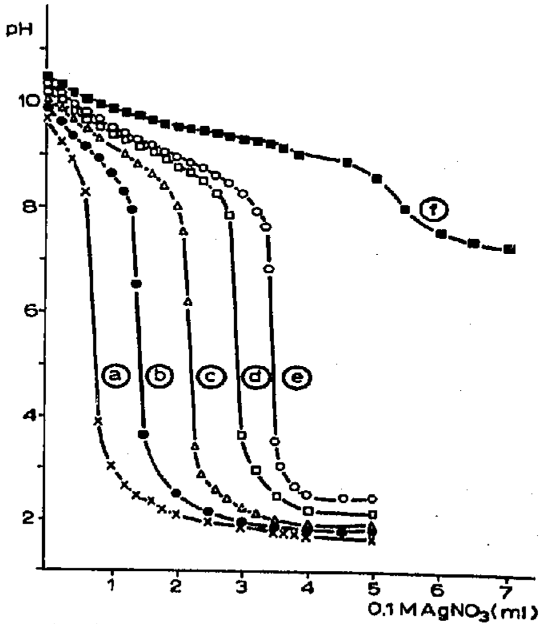
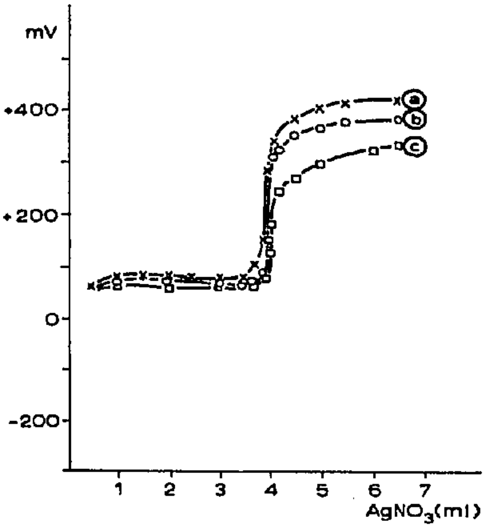


Fig. 8. pH titration curves of 10^{-1} *M* thioacetamide in ammonia solution. (a–f) As in Fig. 5.



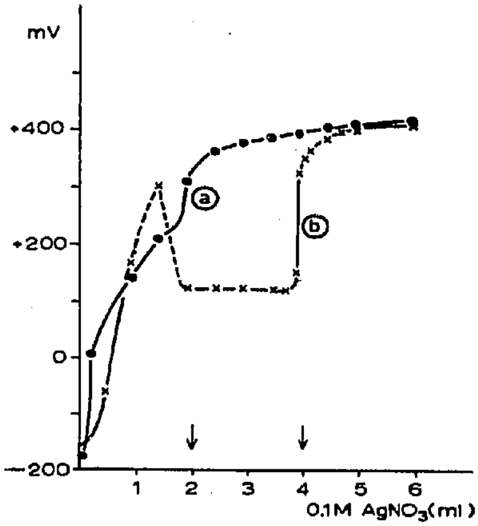
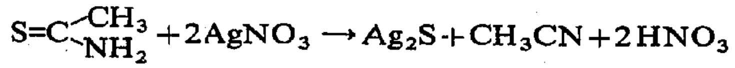


Fig. 9. Potentiometric titration curves of thioacetamide in 10^{-1} *M* acetic acid. (a) 10^{-1} *M* thioacetamide; (b) 10^{-2} *M* thioacetamide; (c) 10^{-3} *M* thioacetamide.

Fig. 10. Potentiometric titration curves of 10^{-1} *M* thioacetamide in 10^{-1} *M* (b) and $5 \cdot 10^{-1}$ *M* (a) nitric acid.

slightly acidic or alkaline solution, a black precipitate was formed. The precipitate was analyzed and found to be silver sulphide.

It is assumed that acetonitrile and nitric acid are formed during the reaction in addition to silver sulphide. Furthermore, the acetonitrile is assumed to hydrolyse giving ammonium acetate, which then in the presence of the nitric acid formed during the reaction transforms to acetic acid and ammonium nitrate according to the following reaction equations:



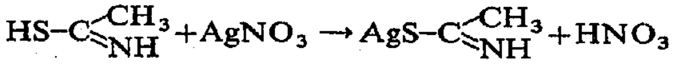
$$S{=}C\begin{matrix}CH_3\\NH_2\end{matrix} + 2AgNO_3 \rightarrow Ag_2S + CH_3CN + 2HNO_3$$

$$CH_3CN + 2\,H_2O \rightarrow CH_3COONH_4$$

$$CH_3COONH_4 + 2\,HNO_3 \rightarrow CH_3COOH + NH_4NO_3 + HNO_3$$

The silver sulphide precipitated in the first step of the reaction was identified by elemental analysis. An ultraviolet spectrum of the filtrate was taken and compared with the spectrum of pure ammonium nitrate, the assumed final product of reaction. The two spectra (Fig. 11) were completely identical.

In 0.5 *M* nitric acid, the reaction of thioacetamide with silver nitrate was entirely different. At a 1:1 molar ratio a light, pearly precipitate was formed. This was identified by elemental analysis and infrared spectroscopy. On this basis the following reaction was assumed to take place in 0.5 *M* nitric acid between the tautomer of thioacetamide and silver nitrate:



$$HS{-}C\begin{matrix}CH_3\\NH\end{matrix} + AgNO_3 \rightarrow AgS{-}C\begin{matrix}CH_3\\NH\end{matrix} + HNO_3$$

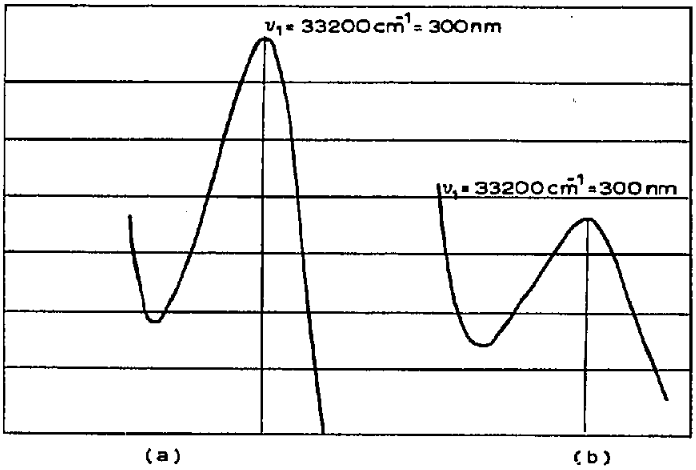


Fig. 11. Ultraviolet spectra of (a) the product of the titration of thioacetamide with silver nitrate formed in addition to silver sulphide; (b) pure ammonium nitrate solution.

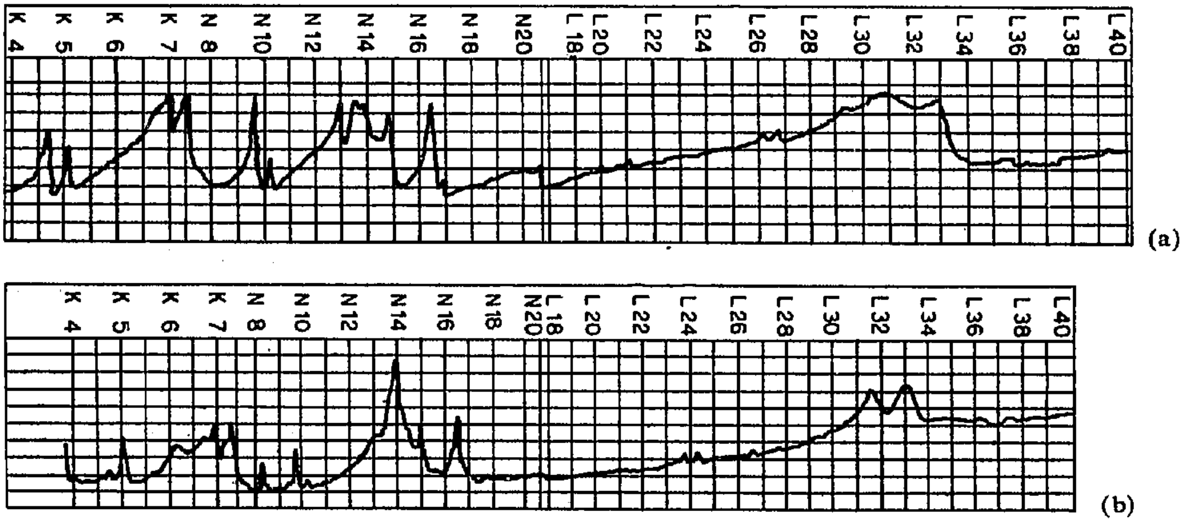


Fig. 12. Infrared spectra of (a) pure thioacetamide; and (b) silver thioacetamide precipitate.

In Fig. 12 are presented the infrared spectra of thioacetamide and of its compound with silver nitrate. The spectra seem to confirm the above reaction, a conclusion also supported by elemental analysis.

SUMMARY

The sulphide ion-selective electrode has been found to be applicable to the determination of thioacetamide in the concentration range of 10^{-1}–10^{-3} *M* by direct potentiometry and titration with silver nitrate. The effects of the acid and alkali content of the solutions on the titration reaction have been studied. In alkaline and slightly acidic solutions the product of the reaction is silver sulphide; in solutions in which the acid concentration exceeds 0.5 *M*, a precipitate of silver thioacetamide is formed. If the alkali concentration of the solution is lower than that corresponding to the amount of acid formed during the titration, another potential jump occurs before the end-point owing to the decrease of sulphide concentration governed by hydrolysis.

RÉSUMÉ

L'électrode sélective ionique au sulfure peut être utilisée pour le dosage de la thioacétamide en concentrations de l'ordre de 10^{-1} à 10^{-3} *M*, par potentiométrie directe et titrage au moyen de nitrate d'argent. On examine l'influence de l'acidité et de l'alcalinité sur la réaction de titrage.

ZUSAMMENFASSUNG

Die sulfidionen-selektive Elektrode kann für die Bestimmung von Thioacetamid im Konzentrationsbereich 10^{-1}–10^{-3} *M* mittels direkter Potentiometrie und Titration mit Silbernitrat verwendet werden. Der Einfluss der Säure- und Alkaligehalts der Lösungen auf die Titrationsreaktion wurde untersucht. In alkalischen und schwach sauren Lösungen ist das Reaktionsprodukt Silbersulfid; in Lösungen, in denen die Säurekonzentration 0.5 *M* überschreitet, entsteht ein Niederschlag von Silberthioacetamid. Wenn die Alkalikonzentration geringer ist, als der während der Titration gebildeten Säuremenge entspricht, tritt vor dem Endpunkt ein anderer Potentialsprung auf, der durch die Herabsetzung der durch Hydrolyse bedingten Sulfidkonzentration hervorgerufen wird.

REFERENCES

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2 S. Y. Shen and M. Kaykaty, *Mikrochim. Acta*, (1971) 96.