

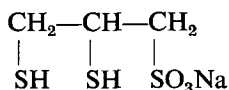
UNITHIOL AS A REAGENT FOR MOLYBDENUM*

A. I. BUSEV, CHANG FAN and Z. P. KUZ'YAEVA
M. V. Lomonosov State University, Moscow, U.S.S.R.

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Summary—Unithiol (sodium 2,3-dimercaptopropanesulphonate) forms coloured complexes with molybdenum in acid solutions. The nature of these complexes is discussed, and it is concluded that Mo^{VI} is reduced to Mo^{V} by the reagent. Coloured complexes contain molybdenum^V and probably molybdenum^{VI}. Unithiol is a promising reagent for molybdenum. It has a high degree of selectivity. Cr and Hg^{II} do not give colours in acidic solution, Hg^{I} gives a greyish-brown precipitate, and Pb^{II} gives a yellow precipitate.

UNITHIOL (sodium 2,3-dimercaptopropanesulphonate)



is a white fine crystalline substance, readily soluble in water and sufficiently stable in solution. Its synthesis has been worked out.¹ Unithiol is used in medicine as an antidote against heavy metal poisoning. As far as can be judged from the first publication,² unithiol is also a valuable analytical reagent.

Unithiol is capable of forming stable complex compounds with a series of metals. The complex compounds of unithiol with some metals are in some cases more stable than the corresponding complexonates. This enables it to be employed for masking when carrying out complexometric determinations, in particular when titrating in an ammoniacal medium.

Quinque- and sexavalent molybdenum (the latter at acidities of pH 4 to 0.5*M* in hydrochloric acid) interact with unithiol in an acidic medium, giving yellow colorations. The colour appears rapidly when the reagent is present in a large excess. The maximum colour is developed on standing for some time. In a neutral or alkaline medium quinque- and sexavalent molybdenum do not form coloured compounds. The optimum optical density of the solutions for molybdate concentrations of 10^{-4} *M* and unithiol concentrations of 10^{-3} *M* is obtained at pH 1.5–2.7.

The absorption curves of the solutions obtained when mixing compounds of quinque- and sexavalent molybdenum with unithiol are shown in Fig. 1. All of the solutions were prepared in the following manner:

The necessary amount of sexa- and quinquevalent molybdenum salt (final molybdenum concentration 10^{-4} *M*) was placed in a 25-ml calibrated flask, then hydrochloric acid was added until the desired pH had been attained. A ten-fold molar amount of the reagent was added and the solution made up to the volume with water. The optical densities of the solutions were determined with respect to water, after 1.5 hr in the case of compounds of molybdenum^V and after 12 hr in the case of compounds of molybdenum^{VI}. Solutions of the reagent alone absorbed practically no light in the region of long wavelengths at which the solutions of molybdenum compounds absorb.

The absorption curve (Fig. 1, curve 1) of solutions of compounds of molybdenum^V exhibits a maximum at 335 $m\mu$. Absorption curves of solutions obtained by mixing

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molybdate with unithiol, also exhibit a maximum at $335\text{ m}\mu$ (Fig. 1, curve 2). When using a hundred-fold molar amount of unithiol the absorption maximum undergoes practically no change. All of these curves have roughly the same region of maximum absorption and, consequently, characterise absorption of the same molybdenum compound.

The coincidence of the absorption curves of compounds of quinquevalent molybdenum with those of compounds obtained starting from hexavalent molybdenum

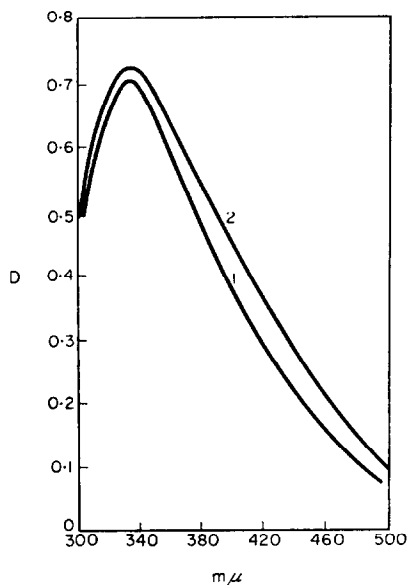


FIG. 1.—Absorption curves of solutions of molybdenum^{VI} and molybdenum^V with unithiol: 1—Molybdenum^V at pH 2; 2—Molybdenum^{VI} at pH 1.52. Concentration of molybdenum^{VI} and molybdenum^V $1.03 \times 10^{-4}M$, concentration of unithiol $10^{-3}M$.

leads to the conclusion that molybdenum^{VI} is reduced by unithiol to the quinquevalent state and that the compounds of molybdenum^V are stable. However, there also undoubtedly exists a compound of molybdenum^{VI} with unithiol.

The apparent molar absorption coefficient of solutions of compounds of quinquevalent molybdenum at $335\text{ m}\mu$ is equal to 7000 (pH 2). The optical density was measured after 1.5 hr. The apparent molar absorption coefficient of solutions obtained by mixing molybdate and unithiol was found to be equal to 7200 at $335\text{ m}\mu$ (pH 1.5, 2 and 2.3). The optical density was measured after 12–15 hr.

The molar ratio in the interaction of molybdenum^V or molybdenum^{VI} was established by the method of isomolar series. Different volumes of a $0.00943M$ solution of sodium molybdate or a salt of quinquevalent molybdenum were mixed with an $0.00943M$ neutral unithiol solution in such a way that the sum of the molar concentrations of the two components in the final solution was always constant and equal to $7.55 \times 10^{-4}M$. The concentration of the unithiol solution was determined by iodometric titration. The acidity was adjusted to pH 2 by the careful addition of a calculated amount of hydrochloric acid. After dilution to the mark with water the pH was checked by means of a glass electrode. The solutions were left to stand for

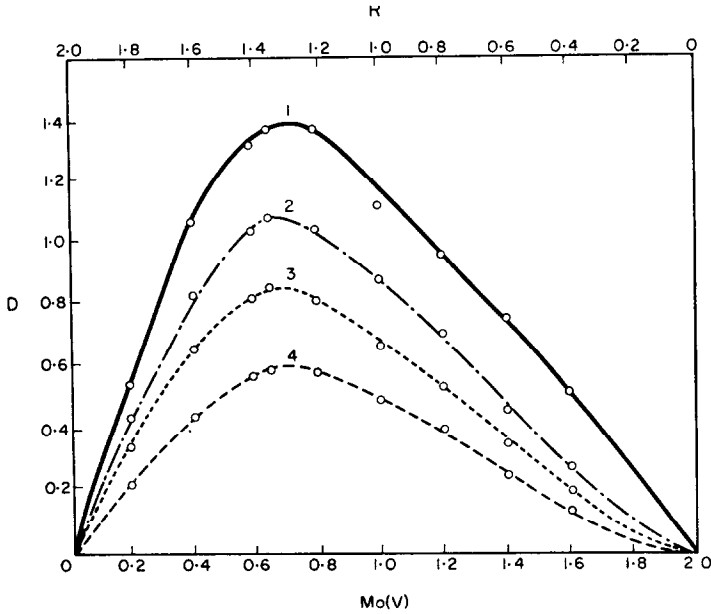


FIG. 2—Molar ratios in the interaction of unithiol with molybdenum^V (pH 2):
 1—335 mμ; 2—370 mμ; 3—430 mμ.
 The optical density was determined 3 hr after preparation of the solutions, with reference to water.

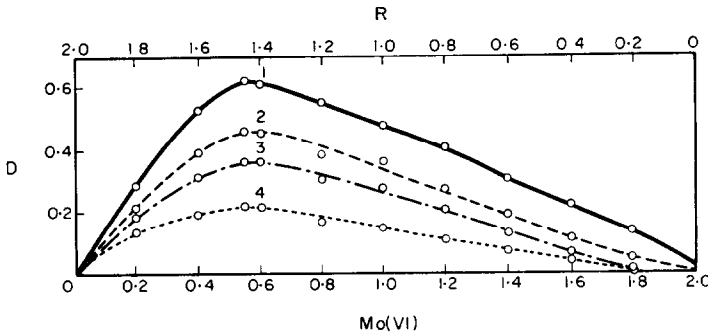
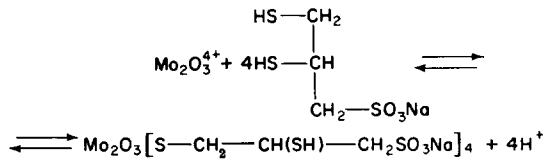


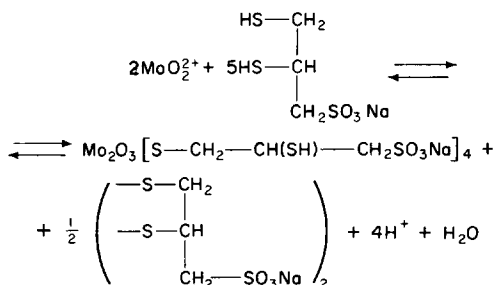
FIG. 3—Molar ratios in the interaction of unithiol with molybdenum^{VI} (pH 2):
 1—335 mμ; 2—370 mμ; 3—390 mμ; 4—430 mμ.
 The optical density was measured 24 hr after preparation of the solutions, with reference to water.

3 hr in the case of molybdenum^V (Fig. 2) or 24 hr in the case of molybdenum^{VI} (Fig. 3). The optical density was measured at 335, 370, 390 and 430 mμ.

Fig. 2 shows that the maximum of the optical density for solutions of the compound of quinquevalent molybdenum and unithiol occurs at a molar ratio of 1:2. On the basis of this, the following equation can be written for the reaction:



The maximum optical density for molybdenum^{VI} at pH 2, occurs at molar ratios of molybdenum to unithiol equal to 2:5 (Fig. 3). This confirms our conclusion that molybdenum^{VI} is reduced to molybdenum^V which also forms a coloured compound with unithiol. Evidently, 2 moles of molybdenum^{VI} are reduced by 1 mole of unithiol to the quinquevalent state and following this 4 moles of unithiol interact with 2 moles of molybdenum^V:



The reduction of sexavalent molybdenum to the quinquevalent state by unithiol was also confirmed by titration with iodine of a mixture of molybdate and unithiol solutions at pH 2. Three solutions containing known amounts of sodium molybdate and an excess of unithiol were prepared in 25-ml flasks. The solutions were prepared in the usual manner and on the next day they were titrated against a 0.01M solution of iodine in the presence of starch. At pH 2, quinquevalent molybdenum is not oxidised by iodine. A gradual weakening of the yellow colour is observed during the titration and close to the end-point the solution is completely colourless. The end-point of the titration is marked by the sharp transition to blue on addition of 1 drop of iodine, which does not disappear for several min. From the amount of iodine required to complete the titration the amount of unreacted unithiol is calculated, and the difference gives the amount of unithiol used in reducing molybdenum^{VI}. Unithiol bound to molybdenum is not oxidised by iodine. Thus, it was established that the reduction of 2 moles of sexavalent molybdenum requires 1 mole of unithiol. The results of the iodometric titration confirm the above proposed scheme for the interaction of unithiol with sexavalent molybdenum.

Unithiol as a reagent for molybdenum has a high degree of selectivity. Chromium and mercury^{II} do not give a coloration with unithiol in an acidic medium, mercury^I gives a greyish-brown precipitate at pH 2 and lead^{II} gives a yellow precipitate.

Thus, unithiol is undoubtedly a very promising reagent for molybdenum.

Zusammenfassung—Unithiol (Natrium-2,3-dimercaptopropansulfonat) bildet in saurem Medium farbige Komplexe mit Mo (V) und Mo (VI). Aus experimentellen Studien wurde geschlossen, dass Mo (VI) durch das Reagens zu Mo (V) reduziert wird. Unithiol ist ein vielversprechendes Reagens für Molybdän und zeigt einen hohen Grad von Selektivität. Chrom und Hg (II) geben keine Färbung in saurer Lösung, Hg (I) gibt einen graubraunen, Pb (II) einen gelben Niederschlag.

Résumé—L'unithiol (2,3-dimercapto-propane sulfonate de sodium) forme des complexes colorés avec Mo (V) et Mo (VI) en solution acide. Les auteurs discutent la nature de ces complexes et concluent que Mo (VI) est réduit en Mo (V) par ce réactif. L'unithiol est un réactif intéressé sant pour le molybdène; il est très sélectif. Le chrome et le mercure (II) ne donnent pas de couleurs en solution acide, le mercure (I) donne un précipité brun grisâtre, et le plomb (II) donne un précipité jaune.

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