MOLYBDENUM ELECTRODE AS INDICATOR ELECTRODE IN COMPLEXOMETRIC TITRATIONS

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Molybdenum electrode has been shown to be a useful indicator electrode for titration of strong as well as weak monobasic acids either with strong or weak base [1,2], of oxidation - reduction [3] and precipitation reactions [4]. Mo/SCE electrode system can be used for the identification of the end point of $I_2/S_2O_3^{2-}$ and $IO_3^-/S_2O_3^{2-}$ titrations but it fails in the detection of the end point in titrations of Fe^{2+} solution with either MnO_4^- or $Cr_2O_7^{2-}$ Mo/Pt bimetallic combination [2] have been successfully used in these redox titrations and also in the titration of Br^- and I^- with Ag^+ using Mo/SCE cell. However, no inflexion was recorded in the titration of Cl^- The present work was undertaken to establish the feasibility of the same electrode is complexometric titrations.

EXPERIMENTAL

Solutions

0.05 M standard EDTA solution.
0.0025 M Hg-EDTA complex solution

Equal volumes of 0.05 M-mercury (II) nitrate (prepared from the A.R. solid) and 0.05 M-EDTA are mixed, the liberated acid is neutralized by the addition of a few drops of 3M - ammonia solution. (In acid solution an insoluble precipitate, probably HgH_2Y, forms after a few days). 10.0 ml of this solution is diluted to 100 ml with distilled water.

Ammonia buffer solution: 20 g. ammonium nitrate and 35 ml concentrated ammonia solution, are mixed and made up to 100 ml with distilled water. 80 ml of this solution is diluted to 1 with distilled water. The pH is about 10.1.

Acetate buffer solution: Equal volumes of 0.5 M-sodium acetate solution and 0.5 M-acetic acid solution are mixed. The resulting solution has a pH of about 4.7.

Approximately 0.05 M solutions of $NiSO_4$, $ZnSO_4$, $CuSO_4$ and $FeNH_4(SO_4)_2$ were prepared and standarised according to recommended procedures [5].

Procedure

Titrations involving both Cu^{2+} and Zn^{2+} solutions were carried out in presence of acetate buffer solution, whereas titrations of Ni^{2+} solutions were carried out in presenoe of ammonia buffer solution. Titration of iron was conducted at pH < 3. Mo wire electrode was used as indicator electrode vs SCE as reference electrode. In case of Cu, Zn and Ni titrations, bimetallic combination electrodes Hg/Mo and also Hg/SCE are also used for comparison. In case of iron titrations Pt/Mo and Pt/SCE are used for comparison.

The Hg indicator electrode for the above experiment was prepared by dipping a pure silver wire in bidistilled mercury for about 5 minutes [6] and used.

In case of titration in alkaline solution, O_2 -free nitrogen gas was bubbled to remove dissolved O_2.

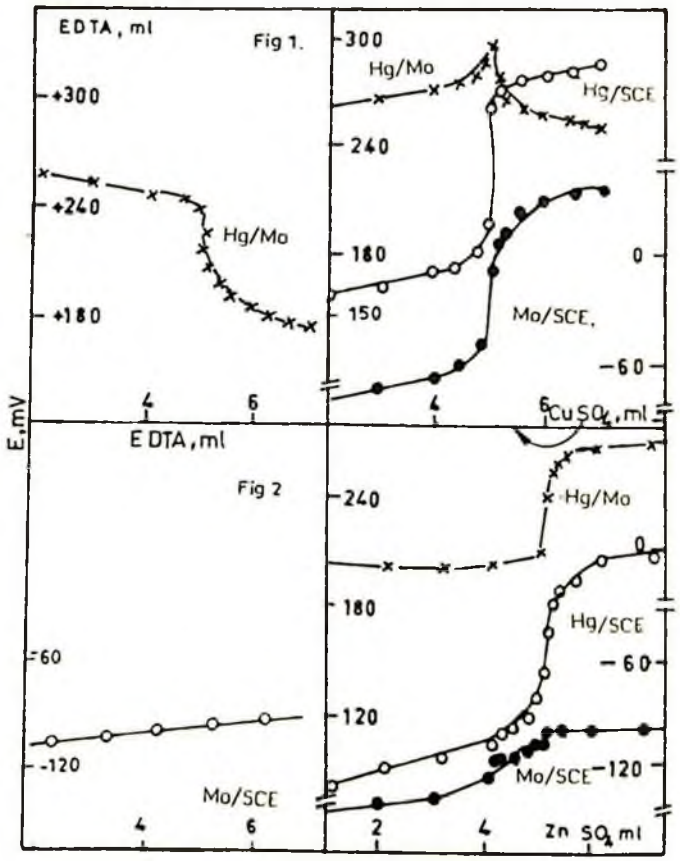


Fig 1&2 Titration curves with 5 ml titrand

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TABLE 1

Values of the potential jumps with different electrode systems

Solution	Potential Jump					
	Mo/SCE		Hg/SCE		Hg/Mo	
	F	B	F	B	F	B
Cu	-20	+60	-40	+60	-30	+30
Zn	- 3	+ 5	-20	+50	-30	+35
Ni	-20	+30	-45	+50	-30	+60
			Pt/SCE		Pt/SCE	
Fe	- 2	+40	-100	+90	-100	+45

* "F" represents titration with EDTA as titrant and "B" represents titration with metal solution as titrant.

Forward titrations, in which EDTA is the titrant, as well as backward titrations in which the cation solution is the titrant, were carried out. Titrations were carried out by placing a known volume of the solution to be titrated, and the same volume of the appropriate buffer and one drop of Hg— EDTA complex, in the titration vessel.

RESULTS AND DISCUSSION

Titration of standard solutions of $CuSO_4$, $ZnSO_4$, $NiSO_4$ and $Fe(NH_4)(SO_4)_2$ with standard EDTA solution showed in general sharp and distinct potential inflexions with Mo/SCE electrodes Figs. (1-4). These potential inflexions coincide with those obtained simultaneously between Hg and SCE electrodes, indicating the feasibility of Mo for end point detection in EDTA potentiometric titrations. It may be noted that the potential inflexions of the backward curves (metal ion as titrant) are more pronounced than those with EDTA as titrant. The end point obtained agree within ±0.1 ml of the titrate with the classical titration with Hg/SCE electrodes. The comparison has been carried out at different concentrations.

In Table (1) are listed the values of the Potential jumps obtained in the various titrations.

It is also noted that in the case of Zn^{++} the end points obtained between Mo and SCE electrodes are not sharp and extend over a range of ca 0.6 ml of the titrant.

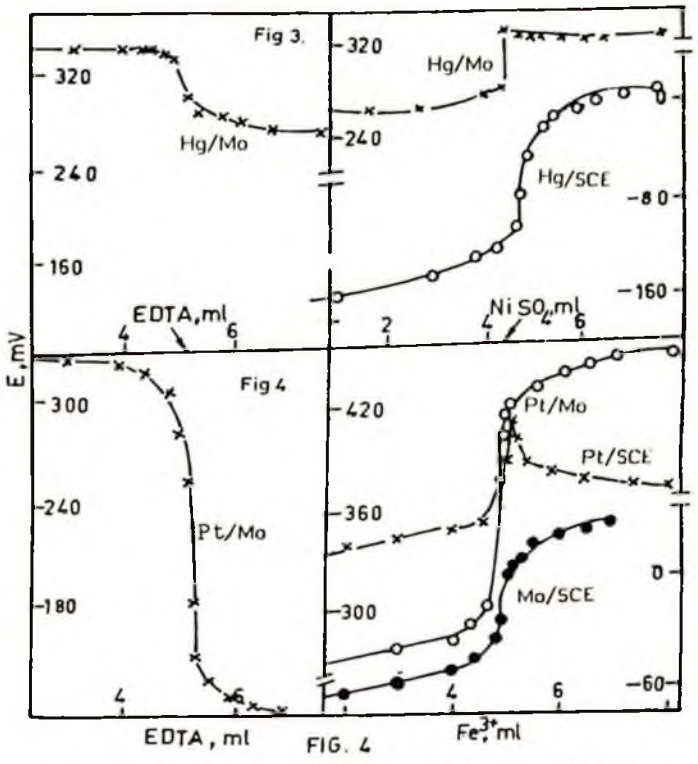


Fig. 3&4 Titration curves with 5ml titrand

However, this difficulty is overcome when the potential difference between Hg and Mo-electrode is considered. In general the potential change at the equivalence points is more sharp and distinct between Hg/Mo bimetallic combination than that measured between Mo/SCE electrodes.

So in such cases Hg/Mo electrodes can be used.

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