Molybdenum Indicator Electrode in Red-ox Titrations

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Molybdenum electrode was used as indicator electrode in iodimetry and iodometry in redox titrations using permanganate or dichronate as titrant. The shape of the titration curve depends on the type of reaction species as well as the manner in which the titration is being conducted.

MO/SCE electrode system can be used for the iodimetry and iodometric titrations. But it fails in the detection of the end point when Fe^{++} solution was titrated either with MnO_4^- or $Cr_2O_7^{2-}$.

MO/Pt bimetallic combination can be used successfully for the redox titration involving Ferrous Sulphate solution.

In previous article [1] the authors reported on the applicability of Mo electrode as an indicator electrode in neutralization titration in aqueous medium. The results obtained reveal that Mo can be used as indicator electrode for the titration of strong as well as weak monobasic acids either with weak or strong base.

The present work was undertaken to establish the feasibility of this electrode for redox titrations.

EXPERIMENTAL

The present study involves the titration of $Na_2S_2O_3$ solutions with I_2 and KIO_3 solutions (iodimetry and iodometry). Examined also the titration of Fe $(NH_4)_2(SO_4)_2$ solutions with either $KMnO_4$ or $K_2Cr_2O_7$ solutions. Forward titration (with oxidant as titrant) as well as backward (with reducing agent as titrant) were carried out. All solutions were prepared from AR materials and doubly distilled water and were standardized according to recommended procedures [2].

The titration vessel was a lipless 100 ml glass beaker. Both Pt and Mo electrodes were mounted into two glass tubings and electrical contact was achieved via thick copper wires fixed to them. These electrodes and a pen type SCE were fixed in a rubber stopper containing central opening for the burette. Titrations were carried out with measurement of the potentials of Mo/SCE, Pt/SCE and Mo/Pt combination to the nearest mV using a PYE precision potentiometer. Experiment were repeated to ensure reproducibility. All experiments were carried out at room temperature (25±2°C).

RESULTS AND DISCUSSION

Typical titration curves obtained with Pt and Mo electrodes are illustrated in Figs. (1 and 2). These curves represent respectively the titration of S_2O_3 with I_2 and IO_3^-, and Fe^{++} with stronger oxidizing agents namely MnO_4^- and $Cr_2O_7^{2-}$. Titration curves of S_2O with IO_3^- are similar to Fig. 1 and those of Fe^{+3} with $Cr_2O_7^{=}$ are similar to Fig. 2. Back titrations in all cases give curves in the reverse direction.

Regarding the change of the potential of Mo/SCE cell during the course of titration a diversity of behaviour was noted. First the shape of the titration curves depends upon the direction in which the titration was carried out, as well as the type of the redox system.

In case of thiosulphate titration, the conventional S type of titration curves are observed with Pt/SCE or Mo/SCE combination but with Mo/Pt combination, a sharp inflection is observed at the end point (Fig. 1).

Different behaviour is noted when Fe^{++} was titrated with MnO_4^- and $Cr_2O_7^{=}$.

Inspection of the curves of Figs. (2) reveals that the potential of Mo electrode, measured relative to SCE, is independent of the addition of the titrant. This may be explained on the following assumption. In the presence of strong oxidizing agents such as MnO_4^- and $Cr_2O_7^{2-}$ the potential of the Mo electrode reaches a value close to that of oxide film formation.

Two different types of titration curves were recognized when Mo/Pt bimetallic combination was used. Titration curves characterized by potential minimum at the stoichiometric end points were

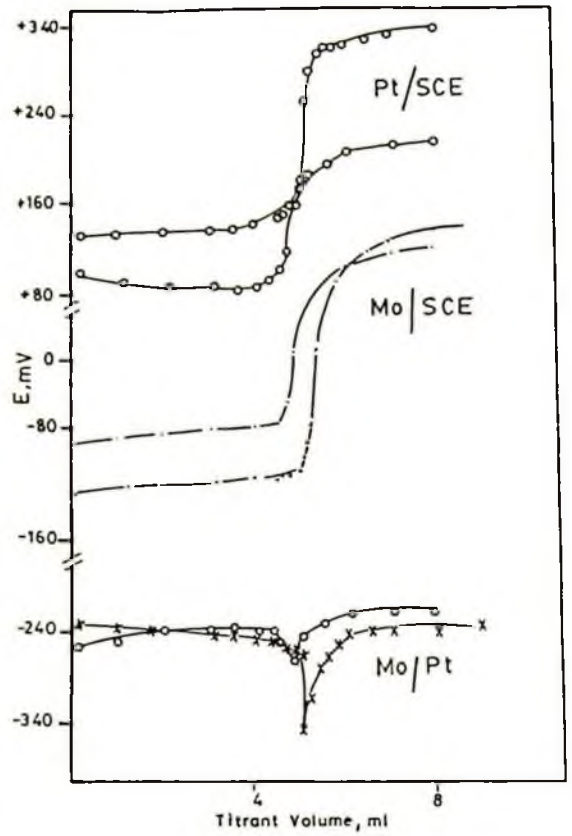


Fig. 1 Titration curves of thio sulphate with iodine. Curve a: Pt/SCE electrodes; curve b: Mo/SCE electrodes curve c: Mo/Pt electrodes

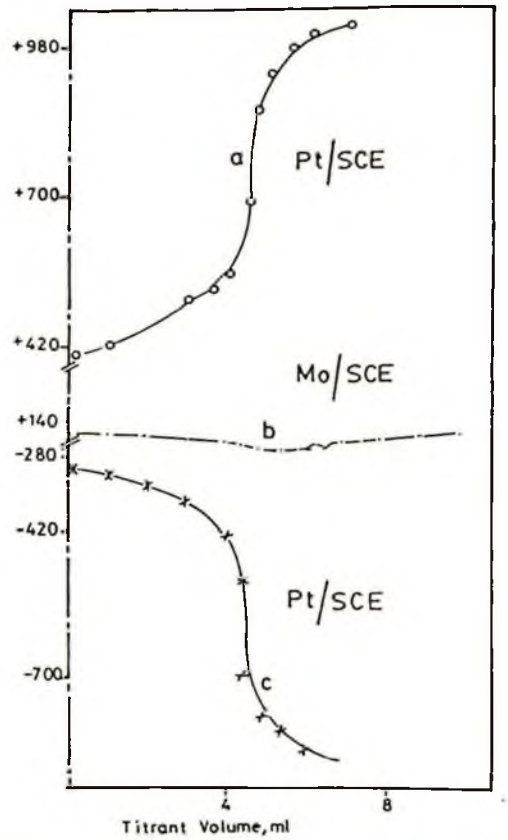


Fig. 2 Titration of Ferrous ammonium sulphate with permanganate: curve a Pt/SCE electrodes, curve b Mo/SCE electrodes curve c Mo/Pt electrodes

obtained when $S_2O_3^{=}$ solutions were titrated with I_2 and IO_3^- solutions whereas S shape titration curves with sharp potential inflexions at the end points were recorded when Fe^{2+} solutions were titrated with MnO_4^- and $Cr_2O_7^{2-}$ solutions.

The calculated value of titrant using the different electrode combination agree well and supports the conclusion that the Mo electrode can given reliable results for such titrations.

Difference in the behavour of Mo and Pt electrodes in the two types of systems may be attributed to the type of charge transfer and/or variations taking place on the Mo-electrode surface [3-5]. However it is beyond the aim of this article to go further in discussing the nature of these variations. From the analytical point of view, the following conclusions can be drawn:

1- Mo/SCE can be used for the identification of the end points of $S_2O_3^{=}$ / I_2 and $S_2O_3^{=}$ / IO_3^- titrations.

2- This couple fails in the detection of end points of the titration of Fe^{2+} with both MnO_4^- and $Cr_2O_7^{2-}$.

3- Mo/Pt bimetallic combinations can be used successfully for the identification of end points of all the studied reactions. However much attention must be paid, since the end point sometimes appears as minimum on the curve and can easily escape notice.

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