SENSITIVE AMPEROMETRIC TITRATION OF o-PHENYLENEDIAMINE EMPLOYING CATALYTIC ELECTRODE REACTION END-POINT DETECTION

E KIROWA-EISNER and HARRY B MARK, JR

Department of Chemistry, University of Michigan, Ann Arbor, Mich 48104 (U S A)

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INTRODUCTION

Certain complexes of metal ions, such as Ni(II), Sn(IV), In(III), Co(II), are reduced at potentials considerably more positive than those observed for the reduction of these metals in non-complexing media[1] (in a *hexaquo* form in non-complexing aqueous media) In some cases, when the concentration of the complexing agent is small compared to the concentration of the metal ion, a polarographic prewave is obtained which is catalytic in nature with respect to the concentration of the complexing agent, as the limiting current is several orders of magnitude greater than the diffusion limiting current for the metal complex Even so, the limiting prewave current is essentially proportional to the concentration of the complexing agent (provided the prewave limiting current is less than about 15% of the main wave limiting current of the uncomplexed metal ion[1,2]) Because of the proportionality of prewave limiting current to concentration of complexing agent and the extreme sensitivity resulting from the catalytic or cyclic behavior of the electrochemical reaction with respect to the complexing agent, these types of metal-complex systems have been employed successfully for the polarographic determination of trace concentrations[1] of the complexing agent. A detailed description of the nature of the electrode reaction and some analytical applications using the prewaves are summarized in previous papers[2,3] It was thought that the catalytic electrode reactions of these metal-complex systems might be employed as end-point detection (or indicator) reactions for sensitive micro-amperometric titrations using these complexing agents.

The o-phenylenediamine (opda)–Ni(II) system was chosen to demonstrate the application of the catalytic prewave as an amperometric end-point indicator, since the catalytic effect of this system is large[1] and the prewave is very well defined (the prewave half-wave potential is over 350 mV more positive than the Ni(II) wave). This paper discusses the analytical applicability and limitations of this system as an amperometric end-point detection system and describes the kinetic complications that arise in the titration of trace concentrations

EXPERIMENTAL

Reagents and apparatus

Analytical-grade reagents were used without further purification Diamino-

phenazine (daph) was prepared by the method of MAYER AND BERENDS[4]. The opda and daph solutions were prepared before each experiment with de-aerated water. A 10^{-2} M Au(III) stock solution was prepared from $AuCl_3 \cdot HCl_3 \cdot 3H_2O$ and was standardized electrogravimetrically[5]. Triple-distilled water was used for the preparation of all solutions. The nitrogen employed for de-aeration was purified by standard procedures.

A three-electrode polarograph, constructed essentially from the operational amplifiers circuits of DEFORD[6], and an Electro Instrument recorder, Model 320, were used for recording polarographic data and the amperometric titration curves.

The dropping mercury electrode had a drop time of 4.30 sec and 1.84 mg/sec outflow of mercury at 52 cm column height in 1.0 M NaOAc, employing an applied potential of -0.8 V vs. Ag/AgOAc (in 1 M NaOAc).

The auxiliary platinum electrode and the reference electrode (Ag/AgOAc, 1 0 M NaOAc) were fitted into separate polyethylene tubes that were filled, respectively, with saturated KNO_3 solution and 1 M NaOAc solution These two polyethylene tubes were inserted into the electrolysis cell and they made contact with the electrolysis solution through Vycor thirsty glass plugs.

The titrant (Au(III) solution) was added to the electrolysis cell by means of a o 2-ml RG micrometer burette (Roger Gilmont).

RESULTS AND DISCUSSION

As has been previously shown[8], NaOAc solution is a suitable supporting electrolyte for the analytical application of the Ni(II)–opda prewave The titrant for opda must react rapidly and completely in this media Two groups of titrants were investigated for the titration of opda The first group, consisting of metals capable of complexing with this compound, was unsatisfactory No suitable reaction system was found, as the values of the stability constants of the metal complexes (from the literature) were not sufficiently large to allow titration of solutions of 10^{-6} M opda The second group consisted of species that were capable of oxidizing opda The choice of a suitable oxidizing reagent depends on the oxidizing "power" as well as on the rate of the oxidation reaction, which is especially important in such dilute solutions Quantitative data on the kinetics of opda oxidation reactions were not available in the literature and thus a trial-and-error testing of a large number of oxidants was undertaken to find a suitable system

A large majority of the common oxidation reagents were found to react slowly Fe(III), Sn(IV), Mn(VII), Cr(VI), Ti(IV), U(III), Hg(II), Ag(I), O_2]. Copper has been reported as a catalyst[7] for the acceleration of some oxidation reactions of opda, but the oxidation rates were not sufficiently fast for a practical titration. Ce(IV) was somewhat faster, but again not sufficiently rapid. However, Au(III) was found to be an excellent oxidizing agent, as the rate of oxidation of opda was found to be very rapid even in dilute solutions.

The titration curve obtained with Au(III) was of unique shape having three well defined "end-point" inflections (Fig 1) During the first portion of the titration (AB), the product of the oxidation reaction increased the rate of the catalytic electrode prewave reaction, as indicated by an increase in the limiting current of the prewave The second portion (line BC) of the titration curve involved a reaction product that

decreased the limiting prewave current. Further addition of titrant beyond the second linear portion of the titration curve (line CD in Fig 1) also decreased the limiting prewave current, but the rate of decrease diminished significantly However, Fig. 1 shows that the overall catalytic effect on the limiting current of the last product of the reaction is still greater than that of the original opda.
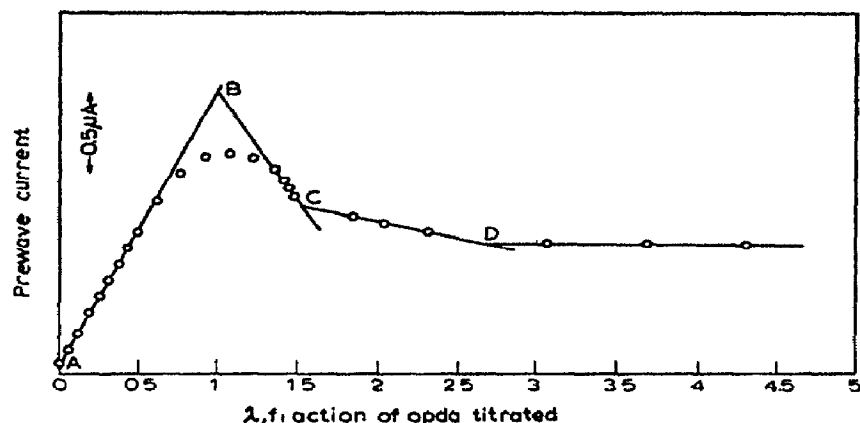

Fig 1 Titration curve of opda with Au(III) λ-mole fraction of Au(III) and initial opda. [opda]= 1 · 10⁻⁶ M, [Ni(OAc)₂] = 2 5 × 10⁻³ M, [NaOAc] = 4 10⁻³ M
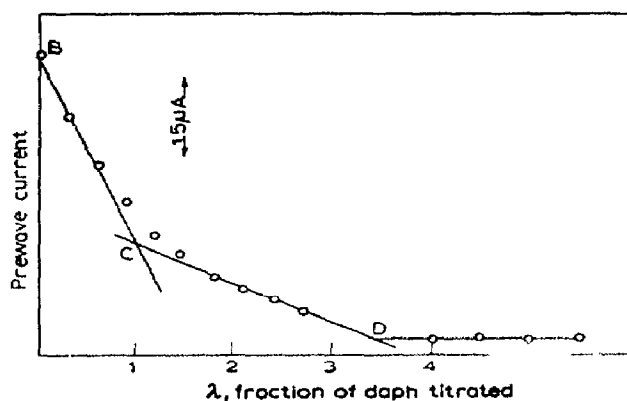

Fig 2 Titration curve of daph with Au(III) λ-mole fraction of Au(III) and initial daph. [daph]= 4 · 10⁻⁶ M, [Ni(OAc)₂] = 7 5 × 10⁻³ M, [NaOAc] = 1 M

The mechanism of the reactions involved in each portion of the titration curve are of considerable interest, as these characteristics were quite unexpected The first portion (AB) of the titration curve corresponds to a 1 1 opda–Au(III) reaction ratio, as the end-point of the inflection occurs when one equivalent of Au(III) has been added to one equivalent of opda Three electrons/molecule of opda are involved in this step, as one equivalent of Au(O) is precipitated

The product of this step (diaminophenazine) was found to be the same as the well known product of the air oxidation of opda[7] This was shown by comparing the behaviour of the product of this titration step with that of a pure daph solution. The two solutions had the same catalytic prewave effect, the same UV and visible spec-
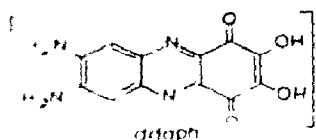
trum, and the amperometric titration curves were of the same shape, as shown in Fig 2.

The second end-point of the titration curve corresponds, approximately, to the completion of a 1 1 daph–Au(III) reaction No precipitate of Au(O) appears during this step (BC in Fig 1 and Fig 2) However, no attempt was made to determine if the product of this step is from (i) a complexation reaction between daph and Au(III), or (ii) a redox reaction in which gold is reduced to a +1 valence state.

The third step of the titration curve (CD in Fig. 1 and Fig. 2) involves the reduction of Au(III) to Au(O). The identification of the final product was carried out by determining the number of electrons involved in the overall reaction, and the elemental composition of the product. This was accomplished by dissolving 0.1000 g of opda in 20 ml water containing 2 g NaOAc Then 30 ml of a 2 5 $\times$ 10^{-2} M Au(III) solution was added slowly (over one hour), from a burette which had its tip immersed in the stirred solution The precipitate formed, which contained the final product plus Au(O), was filtered from the solution (through a fine sintered-glass funnel, which had been previously weighed) and washed with hot dilute hydrochloric acid which dissolved the final product, the gold precipitate was thus isolated on the funnel. The Au(O) was then weighed and the number of electrons involved in the overall reaction calculated from the weight Then NaOAc was added to the solution containing the final product and the reformed precipitate washed with cold water and dried at 130° The product was dark red in colour and was not soluble in common organic solvents

The number of electrons in the overall reaction for the oxidation of one molecule of opda was found to be 8 $\pm$ 0 2 The first product of the oxidation is daph (as shown above) The oxidation of two molecules of opda yields one molecule of daph in a reaction which involves 3 electrons/molecule of opda The further oxidation of one molecule of daph involves 10 electrons (or 8 electrons/molecule of opda to a half molecule of the final product)

From these results it is concluded that the final product is 2,3-dihydroxy-7,8-diaminophenazinchinon-(1,4) or ddaph, which is a 10-electron oxidation product of daph (16 electron oxidation product of 2 opda molecules)

ddaph

The elemental composition of ddaph is C, 52 94%, H, 2 94%, N, 20 6% The elemental analysis of the final product was found to be C, 53 24%, H, 3 16%, N, 20 75%, which is in fair agreement with the calculated values

he recommended titration procedure

The opda (or daph in the mechanism study) solution is transferred into a 50 ml beaker and diluted with Ni(II) and NaOAc (as will be discussed below) Oxygen is then removed by nitrogen An initial polarogram is run, and a voltage on the prewave plateau is chosen for the amperometric titration, or in cases where the concentration of opda is large, the peak potential of the prewave

The titrant is added slowly, with the tip of the burette immersed in the solu-

tion; the solution is stirred thoroughly throughout the titration. If these precautions are not taken, a large localized concentration of oxidant can result in a complete conversion of opda to the final product, ddaph, in this localized volume. The first end-point will, therefore, be premature. During the rising portion of the amperometric titration curve (AB in Fig. 1), the rate of the oxidation reaction is fast and measurement of the currents are taken immediately after the solution is quiescent (a waiting period of 15 sec after stopping the stirring was found to be sufficient). Beyond the first end-point (BC in Fig. 1), the rate of the reaction decreases markedly and, in order to obtain constant current readings, the solution has to be stirred approximately 30 sec after each addition of titrant and then measured after a further 15-sec interval. After the second end-point (CD in Fig. 1), the rate of the reaction again increases and only a 15-sec period for quiescence is required. The overall time for one titration is approximately 35 min if a full curve is required or 25 min for determining the first end-point, which is used for calculating the concentration of opda as the second and the third end-points are not reproducible.

No temperature control is needed, provided no abrupt changes ($\pm 1°$) in temperature occur during a particular titration.

Effect of composition of the supporting electrolyte

The composition and the nature of the supporting electrolyte strongly affect the behaviour of the prewave. As shown previously[2], the catalytic prewave arises from a rate-limiting surface reaction. Thus, the height of the catalytic prewave should decrease with increasing concentration of supporting electrolyte because of the $\psi^°$-effect and the sensitivity of the proposed method can be increased by decreasing the concentration of the supporting electrolyte, NaOAc; $4 \cdot 10^{-2}$ M NaOAc solutions are most suitable for the concentrations of opda in the $1-2 \cdot 10^{-6}$ M range, and 1 M NaOAc for more concentrated solutions.

Effect of nickel ion concentration

As previously shown[8], the prewave limiting current varies linearly with ligand concentrations (at constant Ni(II) concentration) when the ligand concentrations are small compared with the Ni(II) concentration. However, as the concentration of opda becomes comparable with the Ni(II) concentration, a limiting value of the prewave current is reached. The behavior of daph is the same, but the limiting current is reached at lower relative concentrations of ligand (Fig. 3).

When the Ni(II) concentration is increased, three effects are observed: (i) the plateau in Fig. 3 is reached at higher ligand concentrations, which means that the straight part of the curve in Fig. 3 is extended and the titration range of opda is thus extended to more concentrated solutions; (ii) the slope of the straight line portion of the curve in Fig. 3 increases which means that the sensitivity of the prewave (and of the titration) with respect to [opda] is increased; (iii) the overlapping of the prewave with the main wave is increased causing loss of sensitivity and precision.

Because two of these effects are advantageous in practical analyses, the optimum nickel concentration for the titration of different concentrations of opda must be determined as follows: the minimum concentration of nickel is determined by the basic requirement that a linear relationship between the prewave current and the concentrations of opda and daph must be attained, e.g., unless [Ni(II)] is such

that the opda concentrations to be determined, fall on the straight line portions of both curves in Fig. 3 large errors will occur. For example: when $1 \cdot 10^{-5}$ M opda is determined in 7.5×10^{-3} M Ni^{2+}, 1 M NaOAc, the relative error is 1 2% If [Ni(II)] is decreased to 2.5×10^{-3} M, the relative error becomes 30% The upper limit of [Ni(II)] is determined by the overlapping or obscuring of the prewave by the initial
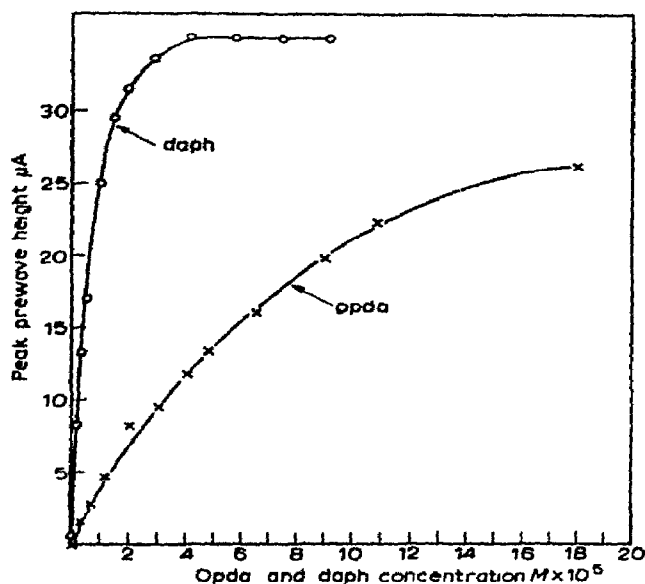

Fig 3 Variation of peak prewave height with concn of opda and daph [Ni(OAc)$_2$] $= 7.5 \times 10^{-2}$ M, [NaOAc] $= 1$ M

rising portion (or foot) of the main wave as mentioned above For example, in the titration of 10^{-5} M opda solution in 4 10^{-2} M NaOAc, the [Ni(II)] has to be decreased to a value of 2.5×10^{-3} M in order to obtain a well defined prewave On the basis of these considerations, the optimum composition of the titrated solution for different opda concentrations was experimentally determined as follows for $2 \cdot 10$ 10^{-5} M opda a 7.5×10^{-3} M Ni(II), 1 M NaOAc solution should be used For $1 \cdot 2$ 10^{-5} M opda, a 2.5×10^{-3} M Ni(II), 4 10^{-2} M NaOAc solution should be used

The upper limit of opda concentration that can be determined in a 7.5×10^{-3} M Ni(II), 1 M NaOAc solution is 10^{-5} M (see Fig 3) For more concentrated solutions of opda, the concentration of Ni(II) must be increased However, it is impracticable to determine solutions of opda more concentrated than $5 \cdot 10^{-5}$ M, as precipitation reactions of the products begin to take place during the titration and interfere with the polarographic waves.

Effects of a maxima suppressor

The prewave exhibits a peak[8] in more concentrated solutions, but not a polarographic maximum. However, the Ni(II) background wave does exhibit a sharp maximum. For the amperometric titration it was found that accurate results could be obtained without a maximum suppressor, but the titrations were usually carried

out in the presence of $4 \cdot 10^{-5}$ M CaOAc (as a maximum suppressor)[6] which decreases the rate of rise and, hence, the overlap of the main Ni(II) wave with the prewave.

Sensitivity and accuracy of the method

The sensitivity of the method is limited by the degree of completeness of the oxidation reaction during the first two steps of the titration. The most dilute solution of opda that was determined experimentally was $1 \cdot 10^{-6}$ M (with a relative standard deviation of 4.6%). In the more concentrated ranges, the accuracy improves as expected ($1 \cdot 10^{-5}$ M solutions of opda were determined with 0.7% relative standard deviation). The quantitative results of typical determinations of various concentrations of opda are summarized in Table I.
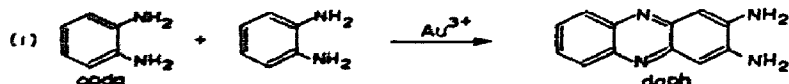
TABLE I

AMPEROMETRIC TITRATION OF OPDA WITH Au(III)

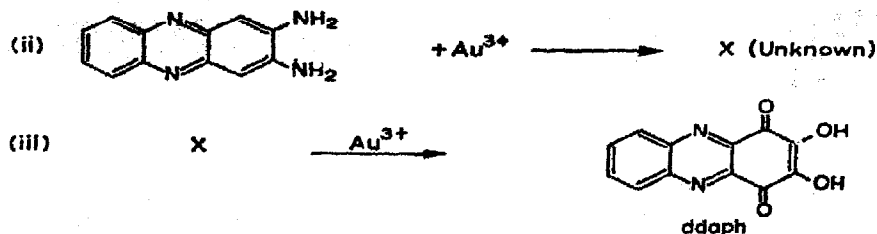| Concn. opda (M $\cdot 10^5$)	Relative standard deviation (%)	Medium composition (M)		
		Ni(OAc)$_2$	NaOAc	Ca(OAc)$_2$
1 0	0 7	7.5×10^{-2}	1	$4 \cdot 10^{-5}$
0 4	1 7	7.5×10^{-2}	1	$4 \cdot 10^{-5}$
0 3	2 3	2.5×10^{-2}	1	$4 \cdot 10^{-5}$
0 2	4.4	2.5×10^{-2}	$4 \cdot 10^{-2}$	0
0 1	4 6	2.5×10^{-2}	$4 \cdot 10^{-2}$	0

Determination of opda in the presence of other isomeric phenylenediamines

Although opda has been succesfully determined polarographically in the presence of the other isomers[9] (employing the Ni–opda prewave), the amperometric titration analysis failed when the other isomers were present In the presence of either or both of the isomers, a very long time is neccessary to reach a steady current after each addition of titrant Slow and competitive side reactions seem to be taking place between the different isomers during the oxidation Furthermore, the end-point is not the true opda equivalence point and is strongly influenced by the composition of the titrating solution and it is therefore impossible to carry out a titration of opda in isomeric mixtures All other species that are readily oxidized by Au(III) also interfere in this titration

SUMMARY

The catalytic prewave of the Ni–opda system has been used for a sensitive amperometric detection of the end-point of the opda titration Au(III) was chosen as titrant from a large group of possible oxidants, because of its favourable equilibrium and kinetic properties Three end-points are observed in the titration and the reactions involved were shown to be as follows

The limiting sensitivity for the determination of opda was found to be $1 \cdot 10^{-6}$ M, with a standard deviation of 4.6%. The titration of opda was not feasible in the presence of the other phenylenediamines. The catalytic electrode reactions involving cyclic regeneration of the redox species, are applicable for end-point detection systems for the amperometric titrations of trace concentration of these species, provided titrants can be found that have suitable thermodynamic and kinetic properties in their reaction with the redox species.

ACKNOWLEDGEMENT

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