Initial Investigations Concerning the Redox Properties of an Iron (III)-Chloro Complex

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Introduction

The Nernst equation always presents difficulties to students because, initially, they are expected to take it on trust; this leads to a certain number of questions regarding its origin, and its derivation may be inappropriate for the course. Ultimately the student may just memorize examples of all the types of calculations for which the equation is used, and then forget them after the final examination. To a teacher this is a major inconvenience because the Nernst equation is a stepping stone to many different experimental examples, and it is a waste of time reteaching it.

Experimental work contained herein formed the basis of a short student research project, and was designed to give the student 'bottom-of-the-ladder' experience with a simple redox reagent not readily available commercially, and also examples of the practical application of the Nernst equation. This experimental work involved the student in selection of a suitable synthetic method for the compound; purification procedures; assay of the compound for iron and chloride; stability studies with both the solid and its aqueous solution; and, finally, a determination of its standard reduction potential potentiometrically having selected an appropriate redox titrant.

The compound itself, tetramethylammonium tetrachloroferrate (III), although having been known for some time (4), has been somewhat neglected analytically. It has been used for studies of conductivity and ultraviolet-visible spectroscopy in non-aqueous solvents (4), and little or no attempt has been made to investigate its redox properties.

Theory

The potential difference between a reference electrode and a suitable indicator electrode throughout a potentiometric titration is governed at all points by the equilibrium ratio of the concentrations of the oxidized and reduced species of the couple. These data may be interpreted theoretically using the Nernst equation (i),

$$E = E^{0'} - \frac{RT}{nF} \ln K \ldots . . (i)$$

where E is the measured potential; $E^{o'}$ is a combination of the standard potential of the reference electrode used and the standard potential of the redox couple; R is the universal gas constant; T is the absolute temperature; n is the number of electrons transferred; F is the Faraday; and K is the equilibrium constant for the reaction.

This equation may be considerably simplified by working at the internationally accepted temperature of 298 K, converting to Briggsian logarithms and calculating the appropriate prelogarithmic constant. It is thus reduced to

$$E = E^{0'} - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \ldots . . (ii)$$

for the reaction

$$Fe^{3+} \text{ (complex)} + e^- \rightleftharpoons Fe^{2+} \text{ (aq.).}$$
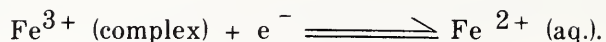
The symbol $[Fe^{3+}]$ has been chosen for brevity to represent the concentration
of the iron (III) complex.

As is usual with these titrations, a plot of potential, E, against volume of
titrant added or fraction of material titrated yields a sigmoidal curve (Figure
1), with the end-point occurring at the inflexion point. If the latter point is measured
accurately, and the standard reduction potential of the titrant is known, that for
the unknown compound may be determined (1). Reference to the paper cited shows
that the theory is a little complex and, in this instance, a simpler approach may
be adopted because the concentration of iron in both forms may be calculated
at any point during the titration. A plot of measured potential against the logarithm
of the ratio of their concentrations yields a straight line, the analysis of which
is much simpler (Figure 2). Both intercepts may be used to calculate a value for
E° as follows: a) along the potential axis the intercept occurs at the point E =
E°'; b) along the abscissa the intercept occurs at E = 0 and E°' is numerically
equal to the logarithmic function at this point (Figure 2). If a value for the stan-
dard potential of the reference electrode is known, a value for the standard poten-
tial of the analyte may be calculated by appropriate addition.

Experimental

1. *Chemicals and Apparatus*

All chemicals used were of analytical grade or better and mixtures of
anhydrous benzene and ethanol were used as solvents.

Excepting the sodium hydroxide standardization, all titrations were monitored

FIGURE 1

POTENTIAL VERSUS SCE (MV)
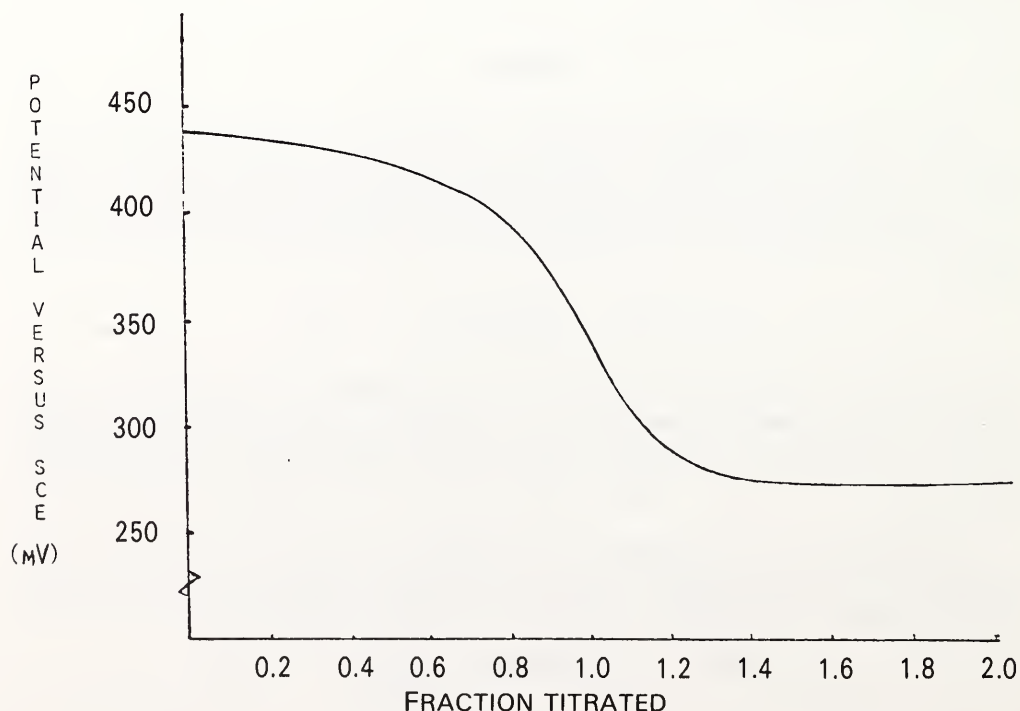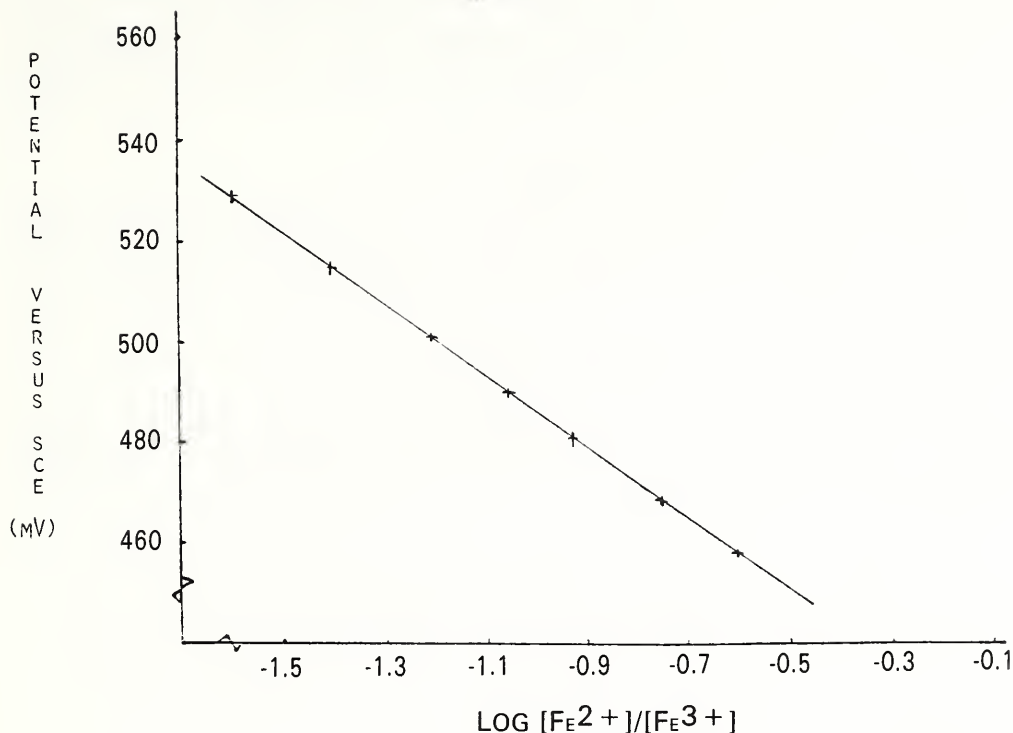
FRACTION TITRATED

FIGURE 2

potentiometrically. The reference was a saturated calomel electrode standardized against a standard hydrogen electrode, and the responsive electrode was a platinum disc. Experiments were conducted in a thermostatted cell at 25.0°C ± 0.1°C and potentials were measured with a Fisher Accumet Model 420 Digital pH/Ion Meter. All glassware was appropriately calibrated by weighing.

2. *Synthesis of Tetramethylammonium Tetrachloroferrate (III) (4)*

Anhydrous ferric chloride (16.25 g., 0.1 mol.) was dissolved in an anhydrous mixture of benzene (100ml) and ethanol (75ml). The solution thus obtained was mixed with one of tetramethylammonium chloride (10.95 g., 0.1 mol.) dissolved in the minimum amount of anhydrous ethanol. The product, an orange-yellow solid, precipitated and was filtered at the pump. It was recrystallized three times from hot ethanol, dried at 110°C and stored in a desiccator over calcium sulfate. A second crop of material could be obtained by evaporation of the mother liquor.

3. *Analysis of the Complex for Iron*

Enough carefully dried potassium dichromate (7) was weighed accurately to make a solution of approximately 0.025 M. Solutions of accurately weighed quantities of the complex were reduced by passage through a Jones reductor, and then titrated with the standard potassium dichromate to either a potentiometric end-point or one of sodium diphenylaminesulphonate (5). Results are contained in Table 1.

4. *Analysis of the Complex for Chloride*

The conventional gravimetric method for chloride with silver ions was rejected in this case because of coprecipitation of ferric hydroxide.

Aliquots of solutions containing accurately known quantities of the complex

were passed through a bed (1 cm² x 30 cm) of Rexyn-100 cation exchange resin in the acid form. The hydrochloric acid produced was titrated with carbonate-free sodium hydroxide solution prepared and standardized in the usual fashion (6). Blank titrations on suitable portions of column effluent were also performed. Results are contained in Table 1.

5. *Determination of Standard Reduction Potential*

Stabilized ascorbic acid solution was standardized iodometrically (2) and was then used to titrate suitable quantities of the complex potentiometrically in acid solution. The results are displayed in Figures 1 and 2, and the data shown in Table 2.

Results and Discussions

Table 1 shows the results of analysis and, within experimental error for the method chosen, the results agree with those obtained theoretically for a substance of composition $(CH_3)_4NFeCl_4$.

TABLE 1: *Results of Iron and Chloride Analysis*

| Species Determined	Result	Standard Deviation
Iron (20.55%)	20.58%	± 0.03%
Chloride (52.17%)	51.8%	± 0.4%

Reference to Figure 1, which shows a typical result, indicates that plots of potential against volume of titrant added yield sigmoidal curves with well-defined breaks. End-points for titrations could be ascertained either by application of the differential method or that of Gran (3). With regard to the determination of standard reduction potential, Figure 2 shows typical results of a titration, the potential with respect to a saturated calomel electrode being plotted against log $[Fe^{2+}]/[Fe^{3+}]$. All lines produced in this fasion were analyzed statistically and correlation coefficients of the order of 0.999 or better were obtained. Calculation results for typical lines are given in Table 2.

TABLE 2: *Standard Potential Determinations*

Nernst Slope (mV)	E-Intercept (mV)	$E_{1/2}ep$ (mV)
-57.5	718	717
-60.2	685	686
-60.8	718	718

Reference to Table 2 shows that the iron (II)-iron (III) couple considered is, to all intents and purposes, perfectly reversible because the Nernst slope is almost exactly that predicted by theory, *ie*: -59.6mV experimentally against -59.1mV theoretically.

Finally, reference to the straight line graphs produced, and statistical analysis of the data yield for the reaction
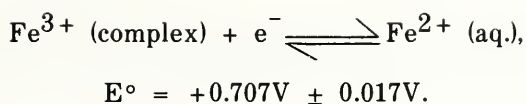
$$Fe^{3+} \text{ (complex)} + e^- \rightleftharpoons Fe^{2+} \text{ (aq.)},$$

$$E° = +0.707V \pm 0.017V.$$

Acknowledgment

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