

NEW INDICATORS FOR OXIDIMETRY

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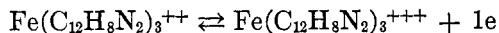
Among the numerous oxidation potential indicators which have been reported, few have had any application to that important branch of oxidimetry which involves strong oxidants. For such use an indicator must have, in addition to the general properties of a good indicator, a high resistance to destruction by irreversible oxidation at high potentials. Otherwise it can only be used when the standard reagent is the oxidizing reagent; back-titration is impossible, and even in the forward titration the indicator is partly destroyed in the regions of local excess and the end point is fleeting. With the noteworthy exception of diphenylamine and its sulfonic acid (3, 4, 5, 6, 7), all oxidation potential indicators that have been reported prior to those which are the subject matter of this paper are so deficient in this important respect that their usefulness is very limited. In addition to this difficulty, there has been an almost complete lack of indicators with color changes in the higher oxidation potential region. Diphenylamine-sulfonic acid changes color at the highest potential,—0.83 to 0.84 volt in sulfuric acid solution against the normal hydrogen electrode (6). This is too low for many titrations, including the very important titration of ferrous iron in the absence of phosphoric acid or fluoride ion.

PHENANTHROLINE-FERROUS ION INDICATOR

The complex ferrous ions of α,α' -dipyridyl and *o*-phenanthroline were discovered and described by Blau (1) in 1898. These ions are readily formed by dissolving the nitrogen base in a nearly neutral water solution of ferrous sulfate. Both possess brilliant red colors, quite similar in quality, and of dye intensity. They are oxidized only by very strong oxidizing agents to substances of a pale blue color. Blau showed that the ferrous complexes were composed of one mole of ferrous ion combined with three moles of the nitrogen base, and that the oxidation process was the

simple conversion to the corresponding ferric complex ion without change of composition. The reaction has been found to be rapid and reversible (8, 10). Moreover the complexes are almost completely resistant to any further oxidation. This resistance is so marked that even acid permanganate solution does not attack them with appreciable rapidity at room temperature. The color change in both cases is completely reversible and of a vividness equal to that of phenolphthalein. In the presence of strong acids both complexes dissociate, but at very different rates, the dissociation of the phenanthroline complex being much the slower.

Attempts to measure the oxidation potential of the reactions by means of titration curves met with good success in the case of the phenanthroline complex, but yielded only very approximate results with the dipyrindyl complex. The difficulty is undoubtedly due to the more rapid dissociation of the latter substance. About all that could be learned from the very erratic data obtained was that the oxidation potential could not be greatly different from that of the phenanthroline reaction. This is further borne out by the behavior of this substance when used as a titration indicator. From the excellent titration curves obtained with the phenanthroline complex it was calculated that the normal oxidation potential of the reaction



in 1 *M* sulfuric acid is 1.14 volts against the normal hydrogen electrode.

Because of the superior stability of the phenanthroline complex, its application as a titration indicator has been studied exclusively. The red color of the ferrous complex is sufficiently vivid so that one drop of 0.025 *M* solution in a volume of 200 cc. gives about the optimum color intensity for this use. When completely oxidized the much less intense blue color of the ferric complex is completely invisible. It therefore functions as a one-color indicator, with the threshold of visibility at about 90 per cent oxidation. The effective oxidation potential of the indicator is therefore about 1.20 volts against the normal hydrogen electrode. This potential is high enough to give a correct end point when iron or even considerably stronger oxidizing agents are titrated. In fact, if the potential were any higher the indicator could not be used for precise titrations with ceric sulfate.

A number of analytical applications have been studied. The indicator has been found to function excellently in simple titrations with solutions of ceric sulfate and potassium dichromate. In a more complicated setting (9, 11) it has been found that in a 5 *M* sulfuric acid solution containing both iron and vanadium, the color change occurs at a potential where iron is completely oxidized, but vanadium is only oxidized to the quadrivalent state. At lower acidities the color change occurs only after both sub-

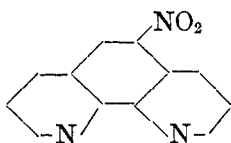
stances are completely oxidized. Very good methods of determining iron and vanadium in the presence of each other and of many normally interfering substances have been worked out.

OTHER INDICATORS OF THE PHENANTHROLINE-FERROUS ION GROUP

The highly desirable properties of phenanthroline-ferrous ion indicator have induced us to search for other indicators of the same type. Our work (2) has been along two lines: the study of other metallic complexes of phenanthroline—Blau described several—and the study of ferrous complexes of nitrogen bases related to phenanthroline.

Investigation of other metallic complexes of phenanthroline has failed to disclose another indicator, although the cobaltous and chromous complexes have interesting properties. They do not, however, possess sufficiently vivid colors.

The preparation of phenanthroline derivatives was at first hampered greatly because of the difficulty and expense of obtaining phenanthroline in quantity sufficient for preparative work. Now that this substance has been made commercially available we expect that this work will be greatly accelerated. Up to the present time we have studied only one such substance. This is a nitration product of phenanthroline, which, from its method of preparation and combustion analysis we judge to be the mononitro derivative



This compound forms a complex ion with ferrous ion, with color properties very similar to the phenanthroline complex. But unlike phenanthroline the complex forms in the presence of considerable concentrations of strong acid. It is oxidized to the same sort of a blue compound, presumably the corresponding ferric ion. We have not been able to make an experimental titration curve. From the behavior of the system when this is attempted we have concluded that this ferric ion is quite unstable. When it is attempted to use this indicator for the titration of iron with ceric sulfate the end point is appreciably late, showing that the oxidation potential is too high for the titration. From the amount of overtitration required to produce the color change we have calculated that the effective oxidation potential must be as high as 1.25 volts in 1 *M* sulfuric acid against the normal hydrogen electrode. This result is extremely interesting, because it shows that the oxidation potential of the ion has been changed by substi-

tution in the organic part. Since there are a large number of such derivatives it seems probable that other indicators of this type will be found, with, we may reasonably hope, oxidation potentials covering a considerable range.

DIPHENYLAMINE DERIVATIVES

We have also investigated the indicator properties of a number of diphenylamine derivatives. The effects of substituting nitro and amino groups were studied.

p-Nitrodiphenylamine is oxidized by strong oxidizing agents to an intensely reddish-violet compound. As an indicator it exhibits most of the peculiarities of diphenylaminesulfonic acid, but is somewhat more reversible. Its oxidation potential is about 0.2 volt higher than that of diphenylaminesulfonic acid. This is high enough so that it serves for the direct titration of iron with ceric sulfate in the absence of phosphoric acid. Results obtained with it for this titration compare very favorably with others obtained with phenanthroline-ferrous ion. It is not sufficiently immune to further oxidation to allow ceric sulfate to be titrated with ferrous sulfate. Nor does it function well when iron is titrated with potassium dichromate, owing to slow reaction. While thus not as good in general as phenanthroline-ferrous ion, it is a much cheaper material and is, within its limitations, an excellent indicator.

All of the six dinitro derivatives which we have studied show no color change even when treated with ceric or permanganate ions or with sodium bismuthate in acid solution; apparently the oxidation potential required is raised so much by the second nitro group that these powerful oxidizing agents are incapable of producing the reaction.

p-Aminodiphenylamine can be oxidized to a reddish-violet compound which can be reversibly reduced to a colorless compound. It is so easily destroyed by the action of excess oxidant that it is not satisfactory as an indicator. It is of interest, however, because its oxidation potential is lower than that of diphenylamine. It was not possible to measure its oxidation potential precisely, owing to the instability of the compound, but it is apparently somewhat below the ferrous-ferric ion potential in 1 *M* sulfuric acid. *p*-Acetylaminodiphenylamine is oxidized by ceric sulfate to a greenish-blue compound which is somewhat more resistant to further oxidation than is the colored compound from the non-acetylated derivative, but still not sufficiently so to be of much use. Its oxidation potential appears to be about 0.06 volt below the ferrous-ferric potential in 1 *M* sulfuric acid.

Strangely enough, 2,4-diaminodiphenylamine is an excellent indicator, quite free from the defects of destruction by excess oxidant. The colored

oxidation product is red, and it is only very slowly destroyed by excess ceric sulfate. The reversibility of the reaction is so good that we were able to make quite good titration curves, both for the oxidation with ceric sulfate and for the reduction with titanous chloride. While these two curves do not agree perfectly, they are good enough to show that both the oxidation and reduction are divalent, and that the oxidation potential in 1 *M* sulfuric acid is 0.70 volt against the normal hydrogen electrode. An indicator in this range, stable toward strong oxidizing agents and strong acids, has not been previously reported.

We have also studied a number of other polyamino derivatives of diphenylamine, but our work has yielded nothing of further interest. Some of these compounds are similar in oxidation potential and behavior to 2,4-diaminodiphenylamine; others are easily destroyed by excess oxidant. The reduction products from 2,4,6-trinitrodiphenylamine and from 2,4,6,3'-tetranitrodiphenylamine show no indicator properties whatever with ceric sulfate.

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