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Diethazine Hydrochloride as a New Redox Indicator in Cerimetric Titration of Fe(II), U(IV), Mo(V), Hydroquinone & Ascorbic Acid

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Diethazine hydrochloride is proposed as a redox indicator in the cerimetric titration of iron(II), uranium(IV), molybdenum(V), hydroquinone and ascorbic acid in sulphuric, hydrochloric and acetic acid media. It gives a sharp reversible colour change at the equivalence point. It has advantages over the existing redox indicators in cerimetry. Its formal redox and transitional potentials are reported.

DIETHAZINE hydrochloride [DH, 10-(2-diethylaminoethyl) phenothiazine hydrochloride] was proposed as a redox indicator for vanadametry[1]. In the present investigation the authors have carried out detailed investigations on the indicator properties of DH in cerimetry and proposed DH as a sensitive indicator in the cerimetric titration of iron(II), uranium(IV), molybdenum(V), hydroquinone and ascorbic acid.

Materials and Methods

DH (0·1 g) was dissolved in distilled water (100 ml) and stored in an amber coloured bottle.

Equimolar vanadate-vanadyl potentiopoised solutions in 0·00625-0·1*M* sulphuric acid were prepared by the method of Smith and Banick[2].

Approximately 0·05*N* and 0·01*N* solutions of Mo(V) in 3*N* hydrochloric acid[3], U(IV) in 2*N* sulphuric acid[4] and hydroquinone[5] were prepared. Molybdenum(V)[6], U(IV)[7,8] and hydroquinone were standardized against standard ceric sulphate solution.

Approximately 0·1*N* ascorbic acid (AR) solution was prepared in doubly distilled water containing EDTA (0·5 g, AR) and formic acid (4 g, AR). The solution was standardized against potassium iodate[9].

Solutions of Ce(IV) sulphate and Fe(II) ammonium sulphate were prepared in 1*N* sulphuric acid solution and standardized by the usual procedures.

The potentiometric assembly consisted of a direct reading potentiometer, a mirror galvanometer, a bright platinum gauze indicator electrode, a saturated calomel reference electrode and an agar salt bridge. The titration mixture was stirred by a magnetic stirrer.

Determination of the formal redox and transition potentials of DH — The formal redox potential of DH was determined by the method of Schilt[10] and potentiopoised method[2]. The transition potentials of DH in the titration of Fe(II) with Ce(IV) sulphate were determined by the potentiometric method[11].

Cerimetric titration of Fe(II), U(IV), Mo(V), hydroquinone and ascorbic acid — 20 ml of 0·05-0·01*N* Fe(II), Mo(V) or hydroquinone, 1 ml of 0·1% DH indicator and phosphoric acid were diluted to 40 ml with sulphuric, hydrochloric or acetic acid. The solution was titrated with 0·05-0·01*N* Ce(IV) sulphate solution to the appearance of pink or orange red colour. In the determination of U(IV) phosphoric acid should be added after the addition of sulphuric acid and 1 ml of 0·1% DH solution to 20 ml of 0·05-0·01*N* U(IV) solution and then diluted to 100 ml with water. The solution was titrated with 0·05-0·01*N* Ce(IV) sulphate. In the titration of 0·1-0·05*N* ascorbic acid, 20 ml of ascorbic acid was diluted to 40 ml with acetic or hydrochloric acid and titrated with Ce(IV) sulphate in the presence of small amount of phosphoric acid using 1 ml of 0·1% DH solution in the beginning for acetic acid and near the end-point for hydrochloric acid. Ascorbic acid was titrated in sulphuric acid medium in the absence of phosphoric acid using 2 ml of 0·1% DH indicator near the end-point. An aliquot of 0·1*N* ascorbic acid solution was diluted to 40/25 ml with phosphoric acid and titrated with 0·1-0·005*N* Ce(IV) sulphate using 1·0-0·5 ml of 0·1% DH indicator in the beginning.

Results and Discussion

The titration conditions, colour changes at the end-points and results are given in Table 1.

The DH indicator is highly soluble in water giving colourless solution which is stable for a longer period at 8° in the dark. It slowly undergoes atmospheric and photochemical oxidation at room temperature which does not in any way interfere in its indicator action. Preliminary experiments have shown that DH undergoes reversible one-electron oxidation to a red intermediate[12,13] which is believed to be a radical cation[14,15]. The red, radical cation is irreversibly oxidized to a colourless sulphoxide[13] with the loss of one more electron. The probable mechanism of oxidation is shown in Chart 1.

Of the three methods used for determining the redox potential of DH the method of Bishop and Crawford[16] could not be successfully applied. Smith and Banick[2] found the formal redox potentials of equimolar vanadate-vanadyl potentiopoised solutions in 0·1-6·0*M* sulphuric acid to be 910-1226 mV and used them for determining the redox potentials of

TABLE 1 — CERIMETRIC DETERMINATION WITH DH INDICATOR

Reductant taken (mg)	Medium	Ce(IV) sulphate (N)	Reductant determined (mg)	Colour change at the end-point
Iron(II)				
113·56	3-6 ml of 10*M* H_3PO_4+0·75-1·75*M* H_2SO_4/ 0·25-1·50*M* HCl/0·50-3·0*M* HOAc	0·1	113·56	Colourless to pink (orange red in 1·0-1·5*M* HCl)
55·75	do	0·05	55·75	
5·68	do	0·01	5·71	
Uranium(IV)				
120·30	0·75-1·5*M* H_2SO_4+2·5-5 ml of 10*M* H_3PO_4	0·05	120·30	Light yellow to orange red
60·58	do	0·05	60·58	
12·03	do	0·01	12·07	
Molybdenum(V)				
193·9	1-3 ml of 10*M* H_3PO_4+0·2-1·0*M* H_2SO_4/ 1·0-1·5*M* HCl/0·5-3·0*M* HOAc	0·1	193·9	Colourless to pink
94·78	do	0·05	94·8	
9·70	do	0·01	9·68	
Hydroquinone				
111·60	2·5-5 ml of 10*M* H_3PO_4+0·5-1·0*M* H_2SO_4/0·6-1·5*M* HCl/0·5-1·0*M* HOAc	0·1	111·60	Light yellow to orange red
55·38	do	0·05	55·40	
5·43	do	0·01	5·47	
Ascorbic acid				
166·2	2-6 ml of 10*M* H_3PO_4+1-2*M* of HOAc	0·1	166·2	Colourless to pink
88·49	do	0·05	88·51	
162·3	2-3 ml of 10*M* H_3PO_4+1-2*M* HCl	0·1	162·3	do
85·4	do	0.05	85·43	
164·38	0 25-0·4*M* H_2SO_4	0·1	164·38	do
82·43	do	0·05	82·45	
164·9	2-4*M* H_3PO_4	0·1	164·9	do
83·59	do	0·05	83·60	
17·60	do	0·01	17·62	do
8·49	do	0·01	8·52	
4·12	do	0·005	4·15	

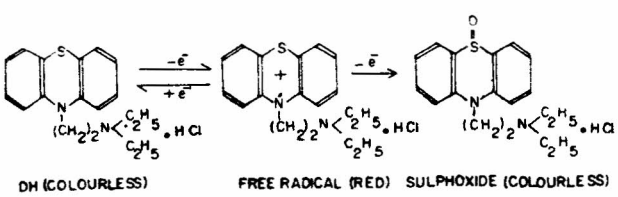

Chart 1

ferroin class of indicators. The DH indicator is immediately oxidized to red colour species by the potentiopoised solutions in 0·1-6·0*M* sulphuric acid indicating that it has the formal potential lower than 910 mV. We have, therefore, determined the potentials of vanadate-vanadyl potentiopoised reference solutions in sulphuric acid concentrations lower than 0·1*M* for finding the formal potential of DH. The potentials of reference solutions are 797, 819, 844, 890 and 908 mV in 0·00625, 0·0125, 0·025, 0·05 and 0·1*M* sulphuric acid respectively. The redox potential of DH has been found to be 900 mV in 0·075*M* sulphuric acid by the potentiopoised method. The potential is accurate within 5 mV.

The formal redox potentials of DH in varying concentrations of sulphuric acid was also determined by the method of Schilt[10] at 20°. A plot of potential in different concentrations of sulphuric acid vs time shows that the formal potential decreases very slightly with increasing time and acid concentration. The potentials (extrapolated to zero time) in 0·25, 0·50, 0·75, 1·00, 1·25 and 1·50*M* sulphuric acid are 856, 845, 834, 825, 810 and 797 ± 5 mV respectively. The transition potentials in 0·75, 1·00, 1·25, 1·50 and 1·75*M* sulphuric acid are 828, 810, 803, 795 and 790 ± 5 mV respectively at 28°. These results show that DH indicator has suitable redox and transition potentials which lie within the potential break in the potentiometric titrations of Fe(II), Mo(V), U(IV), hydroquinone and ascorbic acid with Ce(IV) sulphate in presence of phosphoric acid.

Titration of 0·1-0·01*M iron(II) ammonium sulphate* — The DH indicator does not give sharp end-points in hydrochloric, sulphuric or acetic acid medium because of the slow reduction of red radical cation by Fe(II). However it gives sharp and correct end-points in 0·75-1·75*M* sulphuric, 0·25-1·50*M* hydrochloric or 0·5-3·0*M* acetic acid solution containing 3-6 ml of 10*M* phosphoric acid in a total volume of 60 ml. Sluggish end-points are obtained at acidities higher than 1·75*M* sulphuric or 1·5*M* hydrochloric acid even in the presence of phosphoric acid. Precipitation is seen in acetic acid medium stronger than 3*M*. Phosphoric acid (10*M*) less than 3 ml gives sluggish end-points and more than 6 ml gives premature end-points. The colour change at the end-point is from colourless to pink in sulphuric or acetic acid media and from colourless to pink or orange red in hydrochloric acid media. The end-point colour is stable for 3-6 hr in sulphuric acid and 1·5-3 hr in hydrochloric or acetic acid.

It was found that 0·8-2·0 ml of 0·1% DH solution is necessary in a total volume of 60 ml for proper indicator action. Higher concentration of the indicator gives higher titre values.

The indicator correction needed for DH has been found by comparing the results from the potentio-

metric titrations with those when DH was used. The average indicator correction is 0·02 ml of 0·01*N* Ce(IV) sulphate for 1 ml of 0·1% DH solution.

Preliminary experiments have shown that stannic chloride, mercuric chloride and mercurous chloride do not interfere with the functioning of DH indicator in the titration of Fe(II) with Ce(IV) sulphate. The DH can therefore be usefully employed in the determination of Fe(III) present in ferric alum or haematite after the conventional method of reduction of Fe(III) by stannous chloride.

The DH indicator is superior to ferroin, the most widely used indicator in cerimetry in that it is more sensitive requiring less indicator correction and it works in the presence of acetic acid.

Titration of 0·05-0·01*N uranium(IV)* — Ferroin[17,18], diphenylamine (D)[7], diphenylbenzidine (DB)[7], diphenylaminesulphonic acid (DS)[7], N-phenylanthranilic acid (NPA)[7], copper pthalocyaninetetrasulphonic acid (Cu-PTS)[5], promethazine hydrochloride (PH)[19] and rhodamine 6G (Rh)[20] were proposed as redox indicators in the titration of U(IV) with Ce(IV) sulphate. Willard and Young[17] used ferroin in the titration of U(IV) with Ce(IV) sulphate at 50°. Birnbaum and Edmonds[18] observed that ferroin functioned satisfactorily if U(IV)-Ce(IV) sulphate titration was carried out slowly at 50°. Moreover as ferroin appreciably dissociated at 50° more ferroin was added near the end-point. Ferroin functioned in the titration at room temperature only in 4*N* sulphuric acid solution containing phosphoric acid[21,22]. D, DB, DS and NPA were used in 0·5-1·0*N* sulphuric acid containing phosphoric acid at room temperature. We have observed that phosphoric acid if added in the beginning of the titration, produces turbidity in 0·5-1·0*N* sulphuric acid and forms a gelly 10 min after the completion of the titration.

The DH indicator gives sharp colour change from light yellow to orange red in 0·75-1·50*M* sulphuric acid solution containing 2·5-5·0 ml of 10*M* phosphoric acid in a total volume of 120 ml. At acidities higher than the concentrations of sulphuric and phosphoric acids, given in Table 1, the reduction of the oxidized indicator by U(IV) is slow resulting in the sluggish and premature end-points. The end-point colour is not easily reversible. The stability of the end-point colour increases with decreasing concentration of U(IV) and sulphuric acid. Thus in the titration of 0·05-0·01*N* U(IV), the end-point colour is stable for 6-13 min in 0·75*M* sulphuric acid and 3-8 min in 1·5*M* sulphuric acid.

It was found that 0·8-1·5 ml of 0·1% DH solution is necessary in a total volume of 120 ml for proper indicator action. Higher concentration of the indicator gives premature end-points.

The DH indicator has advantages over ferroin in that it works at lower acidities and requires less indicator correction.

Titration of 0·1-0·01*N Mo(V)* — Ferroin[3,23,24], DB[6], Cu-PTS[5], Rh[20] were proposed as redox indicators in the titration of Mo(V) with Ce(IV) sulphate. Ferroin[23] gave sluggish end-points in 2*N* hydrochloric acid at room temperature in presence of phosphoric acid. It was used in 3*N* hydrochloric acid in presence of syrupy phosphoric acid[6]. Grubitsch *et al.*[25] proposed 4*N* hydrochloric acid for using ferroin indicator. DB acted as an indicator in 4*N* hydrochloric acid. Cu-PTS gave only a pink flash at the end-point.

The DH indicator gives sharp colour change from colourless to pink at the equivalence point in 1-1·5*M* hydrochloric, 0·2-1·0*M* sulphuric or 0·5-3·0*M* acetic acid solution containing 1-3 ml of 10*M* phosphoric acid in a total volume of 60 ml. The indicator gives unstable end-points at higher acidities. 0·8-2·0 ml of 0·1% DH is required for proper indicator action in a total volume of 60 ml. With lower and higher concentrations of DH indicator, the end-points are sluggish. The end-point colour is stable for 20-25 min, in sulphuric or hydrochloric acid medium and for 30-35 min in acetic acid medium.

The DH indicator is superior to the existing redox indicators in that (i) it works at lower acidities, (ii) it is more sensitive requiring less indicator correction and (iii) it functions satisfactorily in acetic acid medium.

Titration of 0·1-0.01*N hydroquinone* — D[26], methyl red[26], ferroin[27], Rh[28], NPA[28], crystal violet[28], alphazurin G[29], *p*-ethoxychrysoidine[30], setopalin[31], eriogreen[31], erioglaucine[31], PH[19] and Cu-PTS[5] were proposed as redox indicators in this titration. The D required large indicator correction to bring the values in agreement with potentiometric values. Methyl red was added near the end-point and the colour change was not satisfactory. Rh, NPA and crystal violet acted satisfactorily in the titration with only 0·05*N* Ce(IV) sulphate. Setopalin, eriogreen, erioglaucine were added in the beginning and near the end-point of the titration and the end-point colour was stable for only a few seconds. It was reported that ferroin[5] needed an indicator correction of 0·1 ml of 0·01*N* Ce(IV) sulphate. Cu-PTS gave only a pink flash at the end-point.

The DH indicator does not suffer from these disadvantages in the cerimetric titration of hydroquinone. It gives sharp and correct end-points in 0·5-1·0*M* sulphuric, 0·6-1·5*M* hydrochloric or 0·5-1·0*M* acetic acid solution containing 2·5-5 ml of 10*M* phosphoric acid in a total volume of 60 ml. It gives a reversible colour change from light yellow to orange red. The end-point colour is stable for 5-6 min. It gives sluggish and premature end-points at higher acidities of sulphuric, hydrochloric and phosphoric acid because of the slow reduction of the oxidized indicator by hydroquinone. Higher concentration of acetic acid leads to precipitation. 0·8-1·5 ml of 0·1% DH are required for proper indicator action in a total volume of 60 ml. With higher concentrations of DH indicator over-titration occurs.

The DH indicator has many advantages over most of the existing redox indicators in that (i) it works in the titration of 0·01*N* hydroquinone, (ii) it is more sensitive requiring less indicator correction, (iii) it works in acetic acid medium and (iv) the end-point colour is more stable.

Titration of 0·1-0·05*N ascorbic acid* — Ferroin, DS NPA and Rh were proposed as indicators in the titration of 0·1*N* ascorbic acid in 0·75-1·50*M*

sulphuric acid solution containing 1 ml of syrupy phosphoric acid[32]. Rh imparted in daylight a greenish florescence which was sharply quenched by slight excess of Ce(IV) sulphate. With ferroin, cerium(IV) sulphate was required to be added in fractions of a drop with the aid of a thin glass rod near the end-point. Experiments have shown that DS and NPA gave varying results with varying concentration of indicators. DH indicator gives sharp colour change from colourless to pink at the equivalence point in 1-2*M* acetic acid solution containing 2-6 ml of 10*M* phosphoric acid in a total volume of 60 ml. The end-point colour is stable for about 25-30 min. Precipitation is seen if the concentration of acetic acid medium is more than 2*M* and less than 1*M*. The indicator gives sharp end-points in 1-2*M* hydrochloric acid in the presence of 2-3 ml of 10*M* phosphoric acid. To get stable and bright end-points 1 ml of the indicator should be added near the end-point. Higher concentrations of phosphoric acid give premature end-points and lower concentrations give sluggish end-points. The end-point colour is stable for about 25 min. The indicator gives sharp colour change in 0·25-0·4*M* sulphuric acid even in the absence of phosphoric acid if 2 ml of 0·1% indicator solution is added near the end-point. Premature end-points are obtained at acid concentrations higher than 0·4*M*. The end-point colour is stable for about 20-25 min.

It was found that 0·8-1·5, 1·0-2·5 and 2·0-3·0 ml of 0·1% DH indicator is necessary in acetic, hydrochloric and sulphuric acid media respectively for proper indicator action in a total volume of 60 ml. Higher concentrations of DH leads to slightly higher titre values.

Titration of ascorbic acid in phosphoric acid medium — Phosphoric acid has some advantages over sulphuric or hydrochloric or acetic acid as titration medium. It reduces the formal potential of Ce(IV)/Ce(III) system to a value of 1·22 V (ref. 33). The redox potential of ascorbic acid-dehydroascorbic acid has been reported to be 185 mV in a solution of *p*H 7 and −12 mV to + 326 mV in a solution of *p*H 8·7-1·05 (ref. 34). This redox potential increases to 445-506 mV in 1-4*M* phosphoric acid[32]. This increased potential affords protection to the ascorbic acid against atmospheric oxidation. Moreover, phosphoric acid complexes any heavy metal ions present which catalyse the atmospheric oxidation of ascorbic acid. Hence very small amounts of ascorbic acid can be determined in phosphoric acid medium. Ferroin[32] was proposed for titration of ascorbic acid in phosphoric acid medium. It functioned only in very high concentration of 12-13*M* phosphoric acid solution. DH indicator gives sharp colour change from colourless to pink at the equivalence point in the titration of ascorbic acid (4-160 mg) with 0·005-0·1*N* Ce(IV) sulphate in 2-4*M* phosphoric acid solution. Below this acidic range premature end-points are obtained. Above this range over-titration occurs. The end-point colour is stable for 35-30 min.

It was found that 0·8-2·0 and 0·4-0·7 ml of 0·1% DH indicator solutions are necessary in the titration with 0·1-0·05*N* and 0·01-0·005*N* Ce(IV) sulphate solution respectively for proper indicator action in a total volume of 60/35 ml.

The DH indicator can be used for the determination of ascorbic acid by Ce(IV) sulphate in the presence of ten-fold excess of oxalic, citric, tartaric, succinic and malic acids, glucose, fructose and sucrose in phosphoric acid medium as these compounds do not interfere. It can also be used in sulphuric, hydrochloric or acetic acid media in the presence of these compounds, except oxalic acid which interferes in the determination.

DH has advantages over NPA and DS in that (i) it gives sharper end-points and more accurate values, (ii) it functions in four acid media while NPA, DS and Rh function only in sulphuric acid medium and (iii) it has less indicator correction. It is superior to ferroin because (i) it works in lower concentration of 2-4*M* phosphoric acid solution, (ii) it functions in hydrochloric and acetic acid media, (iii) it has smaller indicator correction and (iv) it gives sharper end-points.

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