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Prochlorperazine Maleate as a New Redox Indicator in Vanadametry

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Formal and transition potentials of prochlorperazine maleate, a potential indicator in vanadametry have been determined. Titrations of Fe(II), Mo(V), U(IV), Sb(III) and hydroquinone of 0·05 and 0·002*N* have been carried out with sodium vanadate using the indicator in the presence of phosphoric and oxalic acids. Its chief advantages are: (i) it can be used at lower acidities, (ii) the colour change is sharp, (iii) it can be used in microtitrations, and (iv) it has negligible indicator correction.

THERE are only a limited number of redox indicators introduced in vanadametry. These are N-phenylanthranilic acid[1] (NPA), diphenylamine[2] (D), diphenylbenzidine[3] (DB), diphenylaminesulphonic acid[4] (DS), ferroin[5], copperphthalocyaninetetrasulphonic acid[6] (Cu-PTS), neutral red, phenosafranine and safranine[7], dimethylnaphthidinedisulphonic acid[8], iodine monochloride with an extractive end-point[9], chlorpromazine hydrochloride[10] (CPH), promethazine hydrochloride[11] (PH) and 3,4,7,8-tetramethyl-1,10-phenanthroline iron(II) sulphate[12]. We have now investigated the efficacy of 2-chloro-10[3-(4-methyl-1-piperazinyl)propyl]phenothiazine (prochlorperazine maleate, PPM), in the vanadametric determination of Fe(II), Mo(V), U(IV), Sb(III) and hydroquinone. The results are presented in this paper.

Materials and Methods

PPM (0·1 g) was dissolved in hot water, cooled, diluted to 100 ml and stored in an amber coloured bottle.

Approximately 0·05*N* and 0·002*N* solutions of Mo(V)[13], U(IV)[14], Sb(III)[15], hydroquinone[16] and sodium vanadate[17] were prepared. Mo(V)[18] and U(IV)[17,19] were standardized against ceric sulphate. Sb(III) was standardized against potassium bromate[20]. Hydroquinone was standardized against ceric sulphate with a potentiometric end-point[21] and sodium vanadate was standardized against Mohr's salt solution[19].

Solutions of ceric sulphate, ferrous ammonium sulphate, ferroin and NPA were prepared 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 PPM — The formal redox potential of PPM was determined in various concentrations of sulphuric acid by the method of Schilt[22]. The potentials (extrapolated to zero time) in 0·25, 0·50, 1·0 and 1·5*M* sulphuric acid were found to be 795, 766, 748 and 732 ±5 mV respectively. The transition potentials of PPM in the titration of Fe(II) with vanadate were determined by the method described by the authors[10]. In 0·25, 0·5, 1·0 and 1·5*M* sulphuric acid the values of transition potentials are 754, 740, 725 and 720 ±5 mV respectively.

Determination of the sensitivity of PPM towards various oxidizing agents — The sensitivity of PPM towards various oxidising agents were determined by mixing a drop of the test solution containing the oxidant, a drop of 2*N* hydrochloric acid and a drop of 1% PPM solution in a spot plate. Each test was allowed to stand for 30 sec with each oxidant except permanganate where nearly 5 min were required for full development of colour. The sensitivities of the oxidants are in the order of $Ce^{4+} > V^{5+} > Cr_2O_7^{2-} > IO_3^- > BrO_3^- > MnO_4^- > Fe(CN)_6^{3-}$.

Vanadametric determination of Fe(II), Mo(V), U(IV), hydroquinone and Sb(III) — 20 ml of 0·05*N* (or 10 ml of 0·002*N*) Fe(II), Mo(V), U(IV) or hydroquinone, syrupy phosphoric acid, 1·0*N* oxalic acid and 0·1% indicator solution were taken in a conical flask and diluted with sulphuric, hydrochloric or acetic acid to 40 ml (or to 25 ml). The solution was titrated with 0·05*N* (or 0·002*N*) sodium vanadate solution to the appearance of violet (or pink) colour. In the determination of Sb(III), a known amount of $SbCl_3$ was heated with 100% excess of 0·1*N* vanadate in 40 ml of 6*N* sulphuric acid solution at 95-100° for 2-3 min. The solution was cooled and titrated with standardized Mohr's salt solution in the presence of 10 ml syrupy phosphoric acid using 2 ml of PPM indicator near the end-point to the disappearance of violet colour. The details of the titration medium and results were presented in Table 1.

Results and Discussion

The PPM indicator is soluble in water giving colourless solution which is stable for a long time at low temperature (8°) in dark. It slowly undergoes atmospheric and photochemical oxidation at room temperature (25°) after two days which does not in any way interfere in its indicator action. The oxidation of PPM by strong oxidants such as ceric sulphate takes place in two steps. The indi-

TABLE 1 — VANADAMETRIC DETERMINATION WITH PPM INDICATOR

Reductant taken mg	Medium	Normality of vanadate	Reductant determined mg	Colour change
1. 40·8 of Fe(II)	4 ml of syrupy H_3PO_4+0·1 ml of 1*N* $H_2C_2O_4$ +1*N* H_2SO_4/HCl/HAC	0·05	40·8	Greenish blue (parrot green in HCl) through blue to violet
2. 1·78 of Fe(II)	1-4 ml of syrupy H_3PO_4+0·1 ml of 1*N* $H_2C_2O_4$+0·2-0·5*N* H_2SO_4/HCl/0·4-2·0*N* HAC	0·002	1·79	Colourless to pink
3. 65·3 of Mo(V)	0·5-2·0 ml of syrupy H_3PO_4/$H_2C_2O_4$+1·8-2·5*N* H_2SO_4/1·5-2·5*N* HCl	0·05	65·4	Greenish blue through blue to violet
4. 1·48 of Mo(V)	0·5-2·0 ml of syrupy H_3PO_4/1*N* $H_2C_2O_4$ +1-3*N* H_2SO_4/HCl	0·002	1·48	Faint green to light violet
5. 54·0 of U(IV)	2-4 of syrupy H_3PO_4/1-6 ml of 1*N* $H_2C_2O_4$ +1-3*N* H_2SO_4/HCl	0·05	54·0	Parrot green to pinkish green
6. 1·62 of U(IV)	0·5-2 ml of syrupy H_3PO_4/1*N* $H_2C_2O_4$+1-1·5*N* H_2SO_4/HCl	0·002	1·64	Faint green to light violet
7. 20·5 of HQ	2-5 ml of 1*N* $H_2C_2O_4$+1-3*N* H_2SO_4/0·5-2·0*N* HCl	0·05	20·5	Parrot green to pink
8. 1·24 of HQ	1-3 ml of 1*N* $H_2C_2O_4$+0·5-2·0*N* H_2SO_4/HCl	0·002	1·24	Light parrot green to pink
9. 27·5 of Sb(III)	100% excess vanadate + 6*N* H_2SO_4, heat to 95-100° for 2-3 min. Cool, dilute to give 2*N* H_2SO_4+10 ml syrupy H_3PO_4+2 ml PPM near the end-point	[0·05*N* iron(II)]	27·6	Violet through blue to greenish blue
10. 16·9 of Sb(III)	do	[0·05*N* iron(II)]	16·9	do

cator first undergoes a one-electron oxidation to a red intermediate[23,24] which is believed to be a free radical with semiquinonoid structure[25]. The radical is oxidized to a colourless sulphoxide[24] with the loss of one more electron. The probable mechanism of oxidation is shown in Chart 1.

The oxidation of PPM from colourless to red species by vanadate is a reversible process. The speed of oxidation of the indicator increases with increasing acidity and the red colour develops much more quickly in hydrochloric acid medium than in sulphuric acid medium of the same normality. The reduction of the red species of the indicator to a colourless one with reductants is also reversible. The stability of the red colour increases with increasing concentration of acid and with decreasing concentration of vanadate in the solution. When a large excess of vanadate is added, the red colour (appearing violet in the presence of blue vanadyl ions) is gradually destroyed leaving pale blue solution in which it is impossible to get the characteristic violet colour again by the addition of reductant showing that the indicator is irreversibly oxidized to the sulphoxide by a large excess of vanadate. The indicator does not give red colour with V(V) in 1*N* acetic acid even in 30 min. However, a few drops of oxalic or phosphoric acid catalyse the oxidation of PPM to red intermediate in acetic acid medium.

Experiments carried out to determine the concentration of PPM in an actual titration revealed that at least 0·8 ml of 0·1% indicator solution is required in a total volume of 60 ml for proper indicator action. The average indicator correction needed for 1 ml of 0·1% PPM indicator solution is 0·02 ml of 0·01*N* vanadate.

Determination of the formal redox and transition potentials of PPM — The change in colour and composition of a redox indicator takes place at a definite potential. It is therefore, necessary when choosing a redox indicator for a particular titration to ensure that its standard redox potential (E_0) lies within those of the redox systems. Thus E_0 values of Fe(III)-Fe(II)[26], U(VI)-U(IV)[26], Mo(VI)-Mo(V)[27], quinone-hydroquinone[28] and vanadate-vanadyl couples[26] are 0·771, 0·334, 0·48, 0·7 and 0·9994 V respectively. The formal redox potential of the PPM indicator in 1*N* H_2SO_4 is 766 mV which lies between the titrate and the titrant systems. The indicator so selected should have a colour change as close as possible to the equivalence point and the PPM has suitable redox potential which is close to the equivalence potential, (801 mV) of V(V)-V(IV)/Fe(III)-Fe(II) system[10]. Ideally the

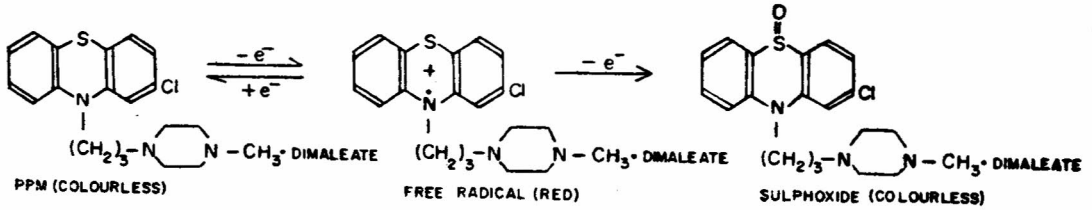

Chart 1

transition potential of a redox indicator should coincide with the equivalence potential in the titration. The transition potential of PPM in 1*N* H_2SO_4 is 740 mV which is close to the equivalence potential of the V(V)-V(IV)/Fe(III)-Fe(II) system. It was found that both formal redox and transition potentials of PPM lie within the potential break; 640-970 mV, in the potentiometric titration of 0·05*N* iron (II) with 0·05*N* vanadate in 1*N* sulphuric acid solution containing 0·5*M* phosphoric acid[29]. Similarly it has been observed that the formal redox and transition potentials of PPM lie within the potential break in the potentiometric titrations of Mo(V), U(IV) and hydroquinone with vanadate.

Titration of Fe(II) ammonium sulphate — The PPM indicator gives sharp end-points in sulphuric or hydrochloric acid media ranging from 0·2-2·0*N* only in the presence of 3-8 ml of syrupy phosphoric acid in a total volume of 60 ml and in acetic acid media ranging from 0·4-4·0*N* in the presence of 5-8 ml of syrupy phosphoric acid. The presence of phosphoric acid results in a very high potential break at the equivalence point and lowers the formal potential of the Fe(III)-Fe(II) couple by complexing with Fe(III) more strongly than with Fe(II)[10]. End-point becomes sharper in the presence of 2 drops of 1*N* oxalic acid which acts as an indicator catalyst. Premature end-points are obtained at higher concentrations of sulphuric, hydrochloric, acetic or phosphoric acid. The colour change at the end-point is from greenish blue → blue → violet in sulphuric and acetic acid media and from parrot green → blue → violet in hydrochloric acid media. The violet colour obtained at the equivalence point is stable for more than 30 min.

Titration of 0·002*N Fe(II) ammonium sulphate* — Contrary to Stiepin's observations[30], the authors found that NPA gave sluggish end-points consuming more vanadate. The PPM indicator works satisfactorily in the titration of very dilute Fe(II) solutions with 0·002*N* vanadate. It gives sharp end-points under conditions given in Table 1. The colour at the end-point is stable for about 1-5 min, depending upon the concentration of oxalic acid. Higher is the concentration of oxalic acid, lower is the stability of the pink colour.

The PPM indicator is far superior to NPA, the most widely used redox indicator in vanadametry because, (i) it works at lower acidities, (ii) it works in acetic acid media, (iii) it is a more sensitive indicator for the microtitrations of Fe(II) with 0·002*N* vanadate, (iv) the colour change is very much sharper and (v) the colour at the end-point is more stable.

Titration of Mo(V) — D[31], DB[17], DS[31], NPA[17,32,33], Cu-PTS[6] and CPH[10] have been recommended as redox indicators for the titration of Mo(V) with vanadate in varying concentrations of sulphuric and hydrochloric acid. All these indicators except CPH function in high concentrations of acid.

The PPM indicator forms white precipitate or turbidity with Mo(VI) and not with Mo(V) in sulphuric acid media ranging from 0·1-1·5*N* and in hydrochloric acid media ranging from 0·1-1·0*N*. However, the precipitate is soluble in higher concentrations of acid.

Vanadium(IV) exerts a retarding effect on the oxidation of PPM with V(V), the magnitude of which decreases with increasing concentration of sulphuric or hydrochloric acid. Phosphoric or oxalic acid catalyses the oxidation of PPM with V(V). The reduction of the oxidized form of the indicator by Mo(V) is fast in solutions of lower acid concentrations and slow in solutions of higher acid concentrations. Molybdenum(VI) and V(IV) catalyse the reduction of the red radical by Mo(V), the combined catalytic effect being more than that of either substance acting individually. In this titration phosphoric or oxalic acid acts as an indicator catalyst. The stability of the colour at the end-point in the presence of phosphoric acid (0·5-2·0 ml) is the same as in the titration of Fe(II). But in the presence of oxalic acid (0·5-2·0 ml) the colour is stable for about 3-5 min. The behaviour of the indicator is similar to that observed in the titration of Fe(II) at acidities higher than the acid concentration given in Table 1. It is found that the PPM indicator functions satisfactorily in the titration of very dilute Mo(V) solutions also.

Titration of U(IV) — D[34-36], NPA[37], CuPTS[6], and PH[11] have been proposed as redox indicators for the titration of U(IV) with vanadate in varying concentrations of sulphuric or hydrochloric acid. All these indicators except PH work only at higher acidities.

The PPM indicator gives sharp colour change only in the presence of phosphoric or oxalic acid because the reduction of the coloured oxidized form of the indicator by U(IV) is induced by the reaction between U(IV) and V(V) only in the presence of phosphoric or oxalic acid. The behaviour of the indicator is the same as that observed in the titration of Fe(II) and Mo(V) at acidities higher than the acid concentration given in Table 1.

The PPM indicator functions satisfactorily in the titration of very dilute U(IV) solutions.

Determination of Sb(III) — Antimony(III) cannot be titrated directly with vanadate either in the cold or in the hot (50°C) as the reaction is not rapid.

Osmium tetroxide, copper sulphate and silver sulphate fail to exhibit any catalytic effect on the reaction in the cold. The rate of oxidation of Sb(III) increases with increasing concentration of sulphuric acid and increasing time of reaction. Preliminary experiments showed that Sb(III) is quantitatively oxidized to Sb(V) if the sulphuric acid concentration is 6-12*N*, the excess vanadate is 75-150% and the time taken is 2-10 min at 95-100°. Hence excess vanadate is added and back titrated with Fe(II). The indicator should be added near the end-point (after 96% titration). It gives sharp colour change from violet → blue → greenish blue.

Titration of hydroquinone — D[28,38], NPA[38], PH[11] and CPH[15] have been used as redox indicators in the titration of hydroquinone with sodium vanadate. DB and NPA are unsatisfactory because they give sluggish end-points and NPA functions only at higher acid concentrations. The redox potential difference between the hydroquinone-

quinone and the vanadate-vanadyl systems indicates that the reaction between hydroquinone and vanadate is likely to be fast. However, the titration of hydroquinone with vanadate using PPM indicator has not been found feasible in sulphuric or hydrochloric acid media ranging from 0·5-5·0*N*. This is due to the retardation of the reaction between the indicator and vanadate by the quinone and V(IV) formed in the reaction. The magnitude of retardation by quinone and V(IV) increases with increasing concentration of quinone and V(IV), the combined effect being more than that of either quinone or V(IV) acting individually. Oxalic acid counteracts the retardation and acts as an indicator catalyst. The speed of oxidation of the indicator by vanadate increases with increasing concentration of oxalic acid so that the titration of hydroquinone with vanadate has been carried out in sulphuric or hydrochloric acid media only in the presence of oxalic acid. The colour change is from parrot green→violet in titrations of lower concentrations of hydroquinone (<1 mg/ml). The violet colour is masked and seen as greenish pink in the titrations of higher concentrations of hydroquinone.

The PPM indicator also functions well in titrations of very dilute hydroquinone solutions.

The PPM indicator has advantages over many of the proposed redox indicators in the titration of Mo(V), U(IV) and hydroquinone because it can be used at lower acidities, the colour change is sharper, it can be used in microtitrations and it has negligible indicator correction.

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