ACTA CHEMICA SCANDINAVICA 8 (1954) 1414—1420

The Use of Redox Indicators in Acidimetric Titrations

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It has been shown that weak bases ($pk_B < 10$) can be titrated acidimetrically using indicators consisting of the ceric-cerous redox system plus nitro-ferroin or ferroin. The execution of the titrations requires some skill, but they can be carried out with reasonable accuracy. Of weak bases, acetate ion, succinate ion, and pyridine have been titrated.

In acidimetric or alkalimetric titrations an acid-base system, comprising a weak acid and its corresponding weak base where these are of different colours, is generally used as indicator; with the exchange of protons a structural change takes place. Instead of a simple acid-base system like this, more complicated indicators are sometimes used. As early as 1850 Schwartz[1] added ferric chloride to gallic acid, and used as an indicator a solution of the resulting precipitate in hydrochloric acid. Schwarz recommended this in preference to litmus, which together with other vegetable extracts was generally used at the time in titrations of bases and acids.

A survey of different types of acid-base indicators has been given by Charlot and Bézier[2]. They mention precipitation indicators with a relatively small transition interval at pH ~ 11. These are applicable to the titration of weak acids, the pk_S's of which are about 8 to 9.

The purpose of the present paper is to show that in principle it is possible to use redox indicators in the titration of weak bases, the pk_B's of which are below 10. Redox indicators are normally applied to redox titrations. However, it has previously been shown that in special cases redox indicators can also be used in precipitation titrations (see *e.g.*, Rancke-Madsen[3]), subject to an abrupt change in the concentration of the reduced or oxidized component of a redox system taking place at or sufficiently close to the equivalence point. The acidimetric titrations mentioned below are based on the same principle, with the modification however that a redox system dependent on pH is added besides the redox indicator.

In the present work a ceric-cerous mixture or in some cases ceric salt alone has been used. According to Bowles and Partridge[4] the neutralization of an acid solution of a ceric salt will take the following course: After the neutralization of a strong acid a colloidal solution will be produced, and the precipitation of the ceric hydroxide can be observed at pH ~ 2.6—2.8. Visible precipitation of cerous hydroxide will occur only at pH ~7.1.

The redox potential in a ceric-cerous solution is given by

$$E = E_o + 0.06 \log \frac{[\mathrm{Ce}^{++++}]}{[\mathrm{Ce}^{+++}]}$$

At pH values between *ca.* 2 and 7, $[\mathrm{Ce}^{++++}]$, and not $[\mathrm{Ce}^{+++}]$, of the above equation will be dependent on pH.

E_o is stated [2] to be 1.60 volts in nitric acid medium; generally, E_o is highly dependent on the medium, due to the formation of ceric complexes.

A 0.1 *M* ceric hydrogen sulphate solution, $\mathrm{Ce(HSO_4)_4}$, 0.05 *M* in sulphuric acid, was used at first as the ceric solution. However, owing to hydrolysis this solution was rather unstable, and it was considered inadvisable to acidify the solution further: since the amount of ceric solution added could not be controlled to great accuracy, the acid concentration of the titrant would have varied. Therefore in place of this solution a 0.1 *M* solution of ammonium hexanitratocerate, $\mathrm{(NH_4)_2Ce(NO_3)_6}$, in ethanol was used. This solution is sufficiently stable for a couple of days, but not appreciably longer. During the experimental work a fresh solution (0.28 g $\mathrm{(NH_4)_2Ce(NO_3)_6}$ in 5 ml 96 % ethanol) was prepared every day.

The cerous salt solution was a 0.1 *M* aqueous solution of cerous nitrate, $\mathrm{Ce(NO_3)_3,6H_2O}$.

DETERMINATION OF THE pH-TRANSITION OF VARIOUS INDICATOR SYSTEMS

The indicator systems hereafter denoted by $\mathrm{Ce^{+4} + Ce^{+3}}$ consisted of 1 drop of a solution of a redox indicator + 0.1 ml ceric salt solution + 0.1 ml cerous salt solution. The indicator systems denoted by $\mathrm{Ce^{+4}}$ did not contain any cerous salt solution.

The indicator systems were added to 30 ml water (as described below under a) and b)) or to a dilute solution of sodium hydroxide (c), d), and e)), and titration was carried out until transition of colour was obtained with different 0.1 *N* acids. The titrations require some skill and should in all cases be carried out very slowly and with vigorous shaking, particularly shortly before the transition. The transitions are not reversible. The pH values were measured electrometrically.

a) Redox indicator: 0.025 *M* nitro-ferroin. Colour transition from red (becoming gradually weaker) until the disappearance of the last shade of red.

Indicator system	titrator	determinations of pH					mean value of pH
$\mathrm{Ce^{+4} + Ce^{+3}}$	$\mathrm{HNO_3}$	1.78;	1.82;	1.78;	1.81;	1.80	1.80
$\mathrm{Ce^{+4}}$	»	1.92;	1.92;	1.93;	1.95;	1.90	1.92
$\mathrm{Ce^{+4} + Ce^{+3}}$	$\mathrm{HClO_4}$	1.54;	1.52;	1.54;	1.53;	1.53	1.53
$\mathrm{Ce^{+4}}$	»	1.68;	1.73;	1.70;	1.73;	1.72	1.71
$\mathrm{Ce^{+4}}$	$\mathrm{H_2SO_4}$	1.92;	1.86;	1.88;	1.90;	1.83	1.88

b) Redox indicator: 0.025 *M* ferroin. Colour transition as under a).

Indicator system	titrator	determinations of pH	mean value of pH
$Ce^{+4} + Ce^{+3}$	HNO_3	2.62; 2.60; 2.54	2.59
Ce^{+4}	»	2.70; 2.76; 2.73; 2.76; 2.77	2.74
$Ce^{+4} + Ce^{+3}$	$HClO_4$	2.32; 2.30; 2.36; 2.34; 2.36	2.34
Ce^{+4}	»	2.54; 2.60; 2.55; 2.61; 2.54	2.57
Ce^{+4}	H_2SO_4	2.53; 2.47; 2.46; 2.47; 2.46	2.48

When sulphuric acid is used as titrator, a precipitate is produced, which makes it difficult to observe the transition.

c) Redox indicator: *o*-tolidine, 1 % ethanol solution. Colour transition from yellow (the ceric colour) to green. The transition to a faint green is difficult to observe, and so the determinations are more uncertain than those described under a) and b).

Indicator system	titrator	determinations of pH	mean value of pH
$Ce^{+4} + Ce^{+3}$	$HClO_4$	4.83; 5.02; 4.66; 4.80; 5.00	4.86
Ce^{+4}	»	5.00; 4.84; 5.12; 4.94; 5.00	4.98

d) Redox indicator: *o*-dianisidine, 0.2 % solution in 2 *M* acetic acid. Colour transition (to a faint red) is very difficult to observe (*cf.* c)).

e) Redox indicator: 0.3 *M* potassium iodide + 3 ml 1 % starch solution. Colour transition from colourless to blue.

Indicator system	titrator	determinations of pH	mean value of pH
$Ce^{+4} + Ce^{+3}$	$HClO_4$	3.04; 3.08; 3.07; 3.13; 3.10	3.08
Ce^{+4}	»	3.26; 3.28; 3.25; 3.22; 3.23	3.25

For the second colour transition of starch-iodine (from blue to colourless) non-reproducible pH values of between 2.4 and 2.9 were found.

f) Redox systems other than ceric-cerous are likely to be applicable as indicators. Thus, the indicator system thallic-thallous + potassium iodide, producing reversible and reproducible transitions, seems to be one possibility. The applicability of this and related indicator systems is being studied more closely at present.

THE USE OF THE REDOX SYSTEM CERIC-CEROUS + NITRO-FERROIN OR FERROIN IN CONNECTION WITH THE TITRATION OF WEAK BASES

As the colour transition for a given indicator system occurs within a very small interval of the pH scale, it is possible in principle to carry out direct titrations of suitably weak bases to the pH values corresponding to the equivalence point. However, although the pH-values at colour transitions are certainly reproducible when the same ceric solution is used, with a different ceric solution slightly different pH values are usually found. Since also other conditions (ionic strength, final volume, *etc.*) should be kept fairly constant, this procedure was rejected.

Instead, titrations were attempted in which the weak acid was titrated past the equivalence point to colour transition of one of the indicator systems mentioned above, and then the overtitration corrected by means of a blank experiment. The blank experiments were carried out on pure water, so that the end volume in the titration of the weak base was practically identical with that in the titration of water. The same indicator system was used in both titrations, and these were carried out as uniformly as possible and to the same colour transition.

CALCULATION

The concentrations mentioned in the following all refer to the final volume of the solution. Let the stoicheiometric concentration of the weak base to be titrated be C_B, and a strong acid be added in excess at a total concentration C_t. The actual concentrations of the weak base and its corresponding weak acid may be written [B] and [S], respectively. The base and acid dissociation constants for the base and its corresponding acid are k_B and k_S, respectively.

The hydrogen ion concentration in the final solution must then be as stated in equation (1), for from the strong acid a quantity of hydrogen ions corresponding to (C_B —[B]) are used for the neutralization of the weak base:

$$[H_3O^+] = C_t - (C_B - [B]) + [OH^-] \tag{1}$$

The last term, which originates from the self-dissociation of water, can be neglected under the circumstances in question, *i.e.* $[OH^-]$ is considered negligible, and rearranging (1) we obtain:

$$[B] = [H_3O^+] - C_t + C_B \tag{2}$$

Further

$$C_B = [B] + [S] \tag{3}$$

which together with (2) gives:

$$[S] = C_t - [H_3O^+] \tag{4}$$

If (2) and (4) are inserted in the usual expression for k_S, we get:

$$k_S = \frac{[H_3O^+]\,[B]}{[S]} = \frac{[H_3O^+]([H_3O^+] - C_t + C_B)}{C_t - [H_3O^+]} \tag{5}$$

In the blank experiments, a strong acid is added to pure water; if the stoicheiometric concentration of the strong acid is C_o in the final volume, then we get:

$$[H_3O^+] = C_o \tag{6}$$

since hydrogen ions originating from the self-dissociation of water can also be neglected here.

If $[H_3O^+]$ is the same in the two solutions, (6) can be inserted in (5), and after rearranging, we get:

$$C_t - C_o = \frac{C_o}{k_S + C_o} \cdot C_B = \frac{[H_3O^+]}{k_S + [H_3O^+]} \cdot C_B \tag{7}$$

It follows that the equation

$$C_t - C_o = C_B \tag{8}$$

is valid with an error the absolute magnitude of which is:

$$C_B - \frac{[H_3O^+]}{k_S + [H_3O^+]} \cdot C_B = \frac{k_S}{k_S + [H_3O^+]} \cdot C_B \text{, which is} < \alpha \cdot C_B$$

if $k_S < \frac{\alpha}{1-\alpha} \cdot [H_3O^+]$, which for small values of α is approximately equal to $\alpha \cdot [H_3O^+]$.

Thus equation (8) is valid with a relative error $< \alpha$ on C_B, if

$$k_S < \alpha \cdot [H_3O^+] \tag{9}$$

or

$$pk_S > pH - \log \alpha \tag{10}$$

or

$$pk_B < 14 - pH + \log \alpha \tag{11}$$

If, for instance, an indicator system with a colour transition at pH = 2 is used, and if < 1 % error is required, then (8) may be used for the calculation of the quantity of base, assuming that $pk_B < 10$.

Table 1. Titration of 15.00 ml 0.0998 N CH_3COONa with 0.0928 N H_2SO_4. Indicator system: Ce^{+4} + nitro-ferroin. Uncertainty on the mean value B: $\mu_B = 0.02$ ml. Uncertainty on single determination of A: $\mu_A = 0.05$ ml. Uncertainty on single determination of A−B: $\mu_{A-B} = 0.06$ ml. Uncertainty on single analysis: $\mu = 0.4$ %. Uncertainty on mean value of determinations $\mu_m = 0.2$ %.

Blank test No.	ml H_2SO_4	Deviation (ml)
1	7.47	+ 0.04
2	7.37	− 0.06
3	7.39	− 0.04
4	7.47	+ 0.04
5	7.45	+ 0.02
Mean value: B =	7.43 ml	

Analysis No.	A: ml H_2SO_4	A−B (ml)	% of the theoretical
1	23.51	16.08	99.7
2	23.55	16.12	100.0
3	23.61	16.18	100.3
4	23.50	16.07	99.6
5	23.64	16.21	100.5
6	23.51	16.08	99.7
7	23.49	16.06	99.6
8	23.51	16.08	99.7
9	23.56	16.13	100.0
10	23.47	16.04	99.5
Mean value: A_m =	23.54	Mean value:	99.9

Table 2. Titration of 15.00 ml 0.1 M CH_3COONa. Indicator: n.f. = nitro-ferroin; f. = ferroin. B = mean value of 5 blank experiments. μ_B = uncertainty on the mean value B. A_m = mean value of 10 single determinations A, where A = ml titrator used for direct titration of the sample. μ_A = uncertainty on A. μ_{A-B} = uncertainty on A−B. R = quantity of acetate found (mean value). μ = uncertainty on single analysis. μ_m = uncertainty on mean value of determinations.

CH_3COONa, M =	0.0998	0.0998	0.1002	0.1009	0.1009	0.1009
Indicator	n.f.	f.	n.f.	n.f.	n.f.	f.
Redox system	Ce^{+4}	Ce^{+4}	Ce^{+4}	Ce^{+4}	$Ce^{+4} + Ce^{+3}$	Ce^{+4}
Titrator	H_2SO_4	H_2SO_4	HNO_3	$HClO_4$	$HClO_4$	$HClO_4$
» , M =	0.0928	0.0928	0.1022	0.0966	0.0966	0.0966
B (ml)	7.43	1.38	7.66	6.76	8.16	0.79
μ_B »	0.02	0.04	0.02	0.04	0.06	0.03
A_m »	23.54	17.50	22.36	22.46	23.86	16.45
μ_A »	0.05	0.06	0.04	0.09	0.09	0.08
μ_{A-B} »	0.06	0.07	0.05	0.10	0.11	0.08
R (%)	99.9	100.0	100.0	100.2	100.2	100.0
μ »	0.4	0.4	0.3	0.7	0.7	0.5
μ_m »	0.2	0.3	0.2	0.3	0.5	0.3

TITRATION OF WEAK BASES

The ceric-cerous + nitro-ferroin or ferroin redox system has been tried as an indicator system in connection with the titration of the following weak bases:

acetate ion $pk_B = 9.2$
succinate ion $pk_B = 9.8$
pyridine $pk_B = 8.9$

a) Acetate ion. A 0.1 *M* solution of sodium acetate was prepared by weighing and diluting to a known volume. $CH_3COONa,3H_2O$ *p.a.*, the purity of which had been controlled, was used. To 15.00 ml of this solution 1 drop of redox indicator + 0.1 ml ceric solution were added, and in some cases 0.1 ml cerous solution also. Then titration was carried out with 0.1 *N* strong acid.

As a blank test 30 ml distilled water, to which was added the same quantity of the indicator system, was titrated. The blank endpoint was determined

Table 3. Titration of 15.006 ml 0.0993 M pyridine. Indicator: n.f. = nitro-ferroin; f. = ferroin. Redox system: Ce^{+4}. Titrator: 0.1021 M H_2SO_4. B = mean value of 5 blank experiments. μ_B = uncertainty on the mean value B. A_m = mean value of 10 single determinations A, where A = ml titrator used for direct titration of the sample. μ_A = uncertainty on A. μ_{A-B} = uncertainty on A−B. R = quantity of pyridine found (mean value). μ = uncertainty on single analysis. μ_m = uncertainty on mean value of determinations.

Indicator	n.f.	f.
B (ml)	5.89	0.81
μ_B »	0.04	0.02
A_m »	20.45	15.34
μ_A »	0.09	0.06
μ_{A-B} »	0.09	0.06
R (%)	99.8	99.6
μ »	0.6	0.4
μ_m »	0.3	0.2

as a mean value of 5 determinations, and it was used in all subsequent titrations of acetate ion in the same series of experiments.

An example of a series of experiments is given in Table 1. In Table 2 this series and similar ones are given with the calculated uncertainties. The titrations of acetate ion with perchloric acid using ferroin were particularly difficult and were sometimes unsuccessful; it turned out to be profitable here not to add the indicator system until about three-quarters of the titration had been carried through.

It will be seen from the tables that there was good agreement between the titrations and the theoretical data. The uncertainty of a single determination is in all cases below 1 %, and with a suitable choice of titrator below 0.5 %. Sulphuric acid seems to be the most suitable titrator.

b) Pyridine. Similar series of experiments were carried out with the weak base pyridine. In these experiments a product was used which had been purified several times by distillation and stored over solid potassium hydroxide. Two series are given in Table 3. It will be noted that the results are in reasonable agreement with those described under a); the uncertainty is a little larger, however, and the results a little low, which is probably due to the volatility of pyridine. In this case, as in that of the acetate ion, sulphuric acid seems to be the best titrator.

c) Other weak bases. Succinate ions were titrated, giving results comparable with those described under a). The titration of aniline failed, however — probably owing to traces of impurities in the aniline. Attempt were also made at the titration of formate ions, although *a priori* this base should be considered a little too weak for titration ($pk_B = 10.2$). Thus, a complete series of experiments gave results of a mean value only 95.4 % of the theoretical.

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Received May 28, 1954.