ACTA CHEMICA SCANDINAVICA 9 (1955) 293—298

# On the Use of a Thallic-thallous System as a pH Indicator

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In a former paper Rancke-Madsen, Skarbye-Nielsen and Østergaard [1] have shown that the ceric-cerous redox system on the addition of a suitable redox indicator can be used as pH indicator.

In the present paper it has been shown that an indicator system can be prepared in a similar way by the thallic-thallous redox system upon addition of potassium iodide and starch. The result is an indicator with two transition intervals in the pH scale, one of which is clear, reproducible and reversible. The transitions take place within a narrow pH range. Further it has been shown that this indicator system can be used as an indicator in the titration of carbonate ion as a monovalent base.

## THE INDICATOR SYSTEM

The redox potential in a solution of a thallic + thallous salt is determined by:

$$E = E_o + \frac{0.06}{2} \cdot \log \frac{[Tl^{+++}]}{[Tl^{+}]}$$

$E_o$ is reported [2] to be 1.280 volt. In the above expression $[Tl^+]$ is independent of pH, whereas $[Tl^{+++}]$, owing to the hydrolysis of the thallic ions and a possible precipitation of the sparingly soluble thallic oxide, is strongly dependent on pH (except at low pH values) [2]. It is stated [3] that thallic oxide is precipitated within a pH-range of *ca.* 1—2.5.

A suitable redox indicator must be added to the thallic-thallous system in order that the resulting system may be used as a pH indicator. Potassium iodide + starch proved to be applicable as a redox indicator. On addition of potassium iodide thallous iodide is precipitated, for which reason $[Tl^+]$ in the above expression is dependent on the amount of iodide added; but the resulting $[Tl^+]$ is still independent of pH. Iodide-starch changes from colourless to blue at $E = 0.60$—$0.65$ volt, and again from blue to colourless at $E = ca.\ 0.90$ volt (in both cases at pH = 7) [4].

In the indicator system mentioned here $E$ increases with decreasing pH, and both the transitions mentioned have been observed.

## EXPERIMENTAL

*Solutions:* Thallous nitrate: A 0.060 *M* $TlNO_3$ solution was prepared by dissolving the calculated weight of the salt in an appropriate amount of water.

Thallic nitrate: Thallous nitrate was oxidized with chlorine in a basic solution to yield a precipitate of thallic oxide. This substance was dissolved in concentrated nitric acid, and this solution was diluted such that the resulting solution of thallic nitrate was *ca.* 2 *M* with respect to nitric acid. It was necessary to acidify the solution rather strongly in order to prevent extensive hydrolysis of the thallic ions.

The content of thallic salt in this solution was determined by thiosulphatimetric titration: To 25 ml of the solution 2 g of potassium iodide were added, causing the formation of a dark-coloured precipitate ($\rightarrow TlI + I_3$). Then 2 ml of 1 % starch solution and 15 ml of ligroine were added, after which titration was performed with standard 0.1 *N* sodium thiosulphate until the iodine colour disappeared from the ligroine phase. The advantage of using ligroine (instead of a more dense liquid such as chloroform) is that ligroine is lighter than the water phase, and the precipitate therefore does not interfere with observations made on the top layer. The observation of the transition in this titration is not possible unless ligroine or a similar substance is added. The solution prepared in this way was found to be a 0.0642 *M* $Tl(NO_3)_3$.

Potassium iodide: The concentration of iodide in the *ca.* 0.1 *M* solution used was determined by argentometric titration, using dichlorofluorescein as adsorption indicator.

*Apparatus:* Values of pH and *E* were measured by means of a "pH meter 22" (Radiometer, Copenhagen). Reference electrode: Calomel electrode.

*Experimental technique:* 1) In a 100 ml beaker the following mixture was made: 25 ml water, 3 ml 1 % starch, *ca.* 5 ml 0.1 *M* sodium hydroxide.

2) A thallic nitrate solution was added (from a semi-micro burette), causing the solution to turn deeply yellow. The thallic hydroxide formed must be supposed to be in colloid solution. The pH in this solution was now *ca.* 11—12.

3) Thallous nitrate solution was added (from semi-micro burette).

4) Potassium iodide solution was added (from semi-micro burette), causing the formation of a yellow precipitate of thallous iodide. The solution was a deep yellow.

5) Nitric acid (0.1 *M*) was then added dropwise until the first colour transition (blue iodine-starch colour) was reached. The solution before this transition was yellow and the colour changed from yellow past green to blue. The deep green colour (situated between yellowish green and bluish green) has been regarded as a transition (first transition) in the experiments described in this paper.

6) pH and *E* were measured.

7) Nitric acid (0.1 *M*) was again added dropwise until the blue colour disappeared (second transition).

8) pH and *E* were measured.

## RESULTS

Using the above method, a number of experiments were performed in which the added quantities of thallic and thallous nitrate were constant, but the quantity of potassium iodide was varied. Table 1 shows the mean values found in some series of experiments. On the addition of a very small quantity of iodide (series 1) no transition took place. The addition of a slightly larger quantity of iodide (series 2) produced a just observable — but indistinct — colour transition. It was not until a still larger quantity of iodide (series 3) was added that clear and distinct transitions were observed. The individual experiments in series 3 are recorded in Table 2. The figures in the last four columns refer to the reproducibility of the transitions: When the equivalence point has been determined for the first time, a little 0.1 *M* sodium hydroxide was added, causing the colour to change back. Then some more 0.1 *M* nitric acid was added, and when the transition occurred the pH and *E* values were again

*Table 1. Mean values of pH and E in 1st and 2nd transitions of the indicator system thallic-thallous to which were added potassium iodide and starch.*

The series of experiments were carried out at the temperature $t°$. In all experiments 0.20 ml of 0.0642 *M* $Tl(NO_3)_3$ and 0.20 ml of 0.060 *M* $TlNO_3$ were used. This means that the solution contains 0.02568 milliequivalents $Tl^{+++}$ as oxidizing agent. A 0.01078 *M* KI was used. The *E*-values were corrected in order to have them stated in millivolt relative to the normal hydrogen electrode.

| Series of Expts. | $t°$ | ml KI | = milli-equivalents $I^-$ | 1st transition | | 2nd transition | |
|---|---|---|---|---|---|---|---|
| | | | | pH | *E* | pH | *E* |
| 1 | 22 | 0.20 | 0.00216 | | — | — | — |
| 2 | 25 | 0.40 | 0.00432 | 7.15 | 757 | 3.92 | 1 040 |
| 3 | 24 | 0.50 | 0.00539 | 7.27 | 754 | 3.94 | 1 020 |
| 4 | 22 | 1.00 | 0.01078 | 7.85 | 707 | 3.61 | 1 036 |
| 5 | 22 | 1.50 | 0.01617 | 8.28 | 679 | 3.12 | 1 050 |
| 6 | 22 | 2.00 | 0.02156 | 8.45 | 667 | 2.08 | 1 058 |
| 7 | 25 | 2.25 | 0.02426 | 8.46 | 664 | 1.64 | 1 062 |
| 8 | 25 | 2.30 | 0.02479 | 8.47 | 662 | — | — |
| 9 | 25 | 2.50 | 0.02695 | 8.53 | 659 | — | — |

determined. The first transition proved to be easily reproducible at exactly the same values of pH and *E*; this was the case in all the other series of experiments, in which analogous tests were made. As regards the second transition, this can be satisfactorily reproduced, but it takes place at a higher pH and a lower *E* value. The other series gave the same results. These results may be due to the fact that some iodine is irreversibly oxidized to a higher oxidation number that that of free iodine.

*Table 2. Individual experiments in series No. 3 (*cf. *Table 1).*

The pH and *E*-values at the 1st and 2nd transitions of the indicator system thallic-thallous to which were added potassium iodide and starch are given in the four first columns. The pH and *E*-values in the four last columns refer to the reproducibility of the transitions (*cf.* the text). $t = 24°$. In all the experiments 0.20 ml of 0.0642 *M* $Tl(NO_3)_3$, 0.20 ml of 0.060 *M* $TlNO_3$ and 0.50 ml of 0.01078 *M* KI were used. The *E*-values were corrected in order to have them stated in millivolt relative to the normal hydrogen electrode.

m = mean value. $\mu$ = uncertainty on the single determination. $\mu_m$ = uncertainty on the mean value of the determinations.

| Expt. No. | 1st transition | | 2nd transition | | 1st transition repeated | | 2nd transition repeated | |
|---|---|---|---|---|---|---|---|---|
| | pH | *E* | pH | *E* | pH | *E* | pH | *E* |
| 1 | 7.30 | 750 | 3.93 | 1 022 | — | — | — | — |
| 2 | 7.30 | 750 | 3.80 | 1 039 | — | — | 4.45 | 983 |
| 3 | 7.30 | 752 | 3.78 | 1 037 | — | — | 4.11 | 1 005 |
| 4 | 7.35 | 751 | 3.90 | 1 028 | — | — | 4.18 | 1 008 |
| 5 | 7.21 | 760 | 3.91 | 1 029 | 7.25 | 754 | — | — |
| 6 | 7.17 | 761 | 4.20 | 990 | 7.32 | 750 | — | — |
| 7 | 7.24 | 760 | 4.20 | 983 | 7.27 | 751 | — | — |
| 8 | 7.20 | 760 | 3.91 | 1 022 | 7.21 | 755 | — | — |
| 9 | 7.30 | 749 | 4.00 | 1 020 | 7.25 | 755 | — | — |
| 10 | 7.30 | 750 | 3.81 | 1 030 | — | — | 4.10 | 1 000 |
| m | 7.27 | 754 | 3.94 | 1 020 | 7.26 | 753 | 4.21 | 999 |
| $\mu$ | 0.06 | 5 | 0.15 | 19 | 0.04 | 2 | 0.16 | 11 |
| $\mu_m$ | 0.02 | 2 | 0.05 | 6 | 0.02 | 1 | 0.08 | 6 |

The results of the rest of the series are shown in Table 1. The uncertainty in these series was in no case more unfavourable for the first transition than that stated for series of experiments No. 3. The first transition proved to be distinct, reproducible and reversible all the way through. The second transition on the other hand, became less and less clear. Already in series No. 6 it was difficult to observe when the last blue colouring disappeared. It also became more and more difficult to reproduce the second transition. As the second transition implies that all iodide has been oxidized to free iodine, an excess of iodide ions in proportion to thallic ions will involve that the second transition cannot take place. Thus, the use of more than 2.38 ml of the potassium iodide solution represents an excess, but even the use of 2.30 ml (series No. 8) caused the nonappearance of the second transition.

As will be noticed, the $E$ values at the transitions for all the experiments were higher that those stated in the literature [4] at the transitions for iodine-starch: 0.60—0.65 volt and *ca.* 0.90 volt, respectively. This may be due to the fact that owing to the yellow colour of the solution an excess of acid must be added in order to produce a distinct transition of colour. The excess of acid brings about a lower pH and consequently a higher $E$ value.

In order to investigate the influence of the concentrations of thallic and thallous ions on the results, some series of experiments were performed, the results of which are shown in Table 3. It is seen that particularly the first transition is not greatly influenced by minor alterations of the concentrations mentioned.

*Table 3. The mean values of pH and* E *at the 1st and 2nd transitions of the indicator system thallic-thallous with potassium iodide and starch added.*

$t = 24°$. 0.0642 $M$ $Tl(NO_3)_3$, 0.060 $M$ $TlNO_3$ and 0.01078 $M$ KI were used. The $E$-values have been corrected in order to have them stated in millivolt relative to the normal hydrogen electrode.

| Series of Expts. No. | ml $Tl(NO_3)_3$ | ml $TlNO_3$ | ml KI | 1st transition pH | 1st transition $E$ | 2nd transition pH | 2nd transition $E$ |
|---|---|---|---|---|---|---|---|
| 4 | 0.20 | 0.20 | 1.00 | 7.85 | 707 | 3.61 | 1 036 |
| 10 | 0.30 | 0.30 | 1.00 | 7.87 | 701 | 3.28 | 1 057 |
| 11 | 0.30 | 0.20 | 1.00 | 7.86 | 703 | 3.51 | 1 054 |
| 5 | 0.20 | 0.20 | 1.50 | 8.28 | 679 | 3.12 | 1 050 |
| 12 | 0.30 | 0.20 | 1.50 | 8.20 | 682 | 3.24 | 1 063 |

## TITRATION OF CARBONATE

The indicator system mentioned above (first transition) was tested in the titration of carbonate ion as monovalent (monobasic, monoacid) base:

$$CO_3^{--} + H^+ \rightarrow HCO_3^-$$

The equivalence point is at $pH = \frac{1}{2}(pk_1 + pk_2) = ca.$ 8.3, depending to a certain degree on the ionic strength.

## EXPERIMENTAL

*Solutions:* Sodium carbonate: Dried, anhydrous $Na_2CO_3$ *p.a.* was weighed, and a solution of known concentration was prepared. The concentration was also checked by titration with standard 0.1 *M* nitric acid after carbon dioxide had been boiled out. Result: The solution made was found to be a 0.2471 *M* $Na_2CO_3$.

Nitric acid: The standard solution was a 0.1055 *M* $HNO_3$.

Thallous nitrate, thallic nitrate and potassium iodide: The solutions described earlier in this paper were used.

*Experimental technique:* Since the thallic nitrate solution used for the production of the indicator system is strongly acid, it was necessary to adjust the indicator system at the pH value required (*ca.* 8.3) before the addition of the sample (*in casu* the solution of sodium carbonate).

Production of the indicator system: 25 ml water, 3 ml 1 % starch, *ca.* 5 ml 0.1 *M* sodium hydroxide, 0.20 ml thallic nitrate (*i.e.* 0.013 millimole), 0.20 ml thallous nitrate (*i.e.* 0.012 millimole), and 1.50 ml potassium iodide were, as in the earlier experiments, brought to the first transition by means of 0.1 *M* nitric acid. According to previous experiments pH is equal to 8.28.

10.201 ml of 0.2471 *M* $Na_2CO_3$ was added, after which titration was carried out with 0.1055 *M* $HNO_3$ to the same transition; the end volume was *ca.* 70 ml. In this solution the ionic strength was different from that in the indicator system before the addition of sodium carbonate. An experimental investigation shows that at the equivalence point the pH = 8.20 in the final volume. However, experiments also show that the quantity of acid which has to be used in order to change pH in the solution of the indicator system from 8.30 to 8.10—8.20 is very small and equal to *ca.* 0.02 ml. This means that the error which is made when fixing the solution of the indicator system at pH = 8.28 instead of pH = 8.20 can be considered negligible.

## RESULTS

a) After various experiments the above indicator system was found to be the one that gave the most detectable change of colour at the equivalence point pH = 8.20.

The colour changes were found by fixing the indicator system at pH = 8.28. Then a little 0.1 *M* sodium hydroxide was added. The solution was diluted with water, and then 0.1 *M* nitric acid was added dropwise until the final volume was *ca.* 70 ml. The following colour changes were observed:

| | |
|---|---|
| pH > 8.45—8.50 | yellow |
| pH = 8.45—8.50 | incipient dark-colouring |
| pH = 8.25—8.30 | faint green |
| pH = 8.20 | green (point of equivalence) |
| pH = 8.10 | bluish green |
| pH = 8.00—8.05 | blue |
| pH = 7.90—7.95 | deep blue |

*Table 4. Titration of carbonate ion as monovalent base.*

Indicator system: Thallic-thallous with potassium iodide and starch added. Titrand: 10.201 ml of 0.2471 *M* $Na_2CO_3$. Titrator: 0.1055 *M* $HNO_3$. As real value is considered: 23.89 ml $HNO_3$.

m = mean value. $\mu$ = uncertainty on single determination. $\mu_m$ = uncertainty on the mean value of the determinations.

| Expt. No. | ml $HNO_3$ | Deviation from real value ml | % |
|---|---|---|---|
| 1 | 23.88 | −0.01 | 0 |
| 2 | 23.80 | −0.09 | 0.4 |
| 3 | 24.05 | +0.16 | 0.7 |
| 4 | 23.90 | +0.01 | 0 |
| 5 | 23.83 | −0.06 | 0.3 |
| 6 | 23.94 | +0.05 | 0.2 |
| 7 | 23.68 | −0.21 | 0.9 |
| 8 | 24.08 | +0.19 | 0.8 |
| 9 | 23.75 | −0.14 | 0.6 |
| 10 | 24.14 | +0.25 | 1.0 |
| 11 | 23.90 | +0.01 | 0 |
| 12 | 23.78 | −0.11 | 0.5 |
| 13 | 24.12 | +0.23 | 1.0 |
| 14 | 23.87 | −0.02 | 0.1 |
| 15 | 23.99 | +0.10 | 0.4 |
| 16 | 23.72 | −0.17 | 0.7 |
| m | 23.90 | | |
| $\mu$ | 0.14 | | |
| $\mu_m$ | 0.04 | | |

b) The known solution of carbonate was titrated visually to the above-mentioned green colour. Sixteen experiments were carried out each with the same quantity of carbonate. The results are given in Table 4. Since the solutions were all of the same known concentration, calculations can be made to the effect that 23.89 ml 0.1055 *M* $HNO_3$ is equivalent to the quantity of carbonate used. It will be seen that the mean values of the results of the experiments (23.90 ml) is in good agreement with this, and that the individual results are in the interval 23.89 ml $\pm$ 1 %. Whenever titrations are carried out quickly, there is a tendency to use too much acid, possibly because this causes a local evolution of carbon dioxide from the solution.

The titrations were repeated with new solutions with results corresponding to those mentioned above.

Therefore, the results show that the indicator system in question can be used for the titration of carbonate ion to hydrogen carbonate ion. The method is fairly accurate, but cannot be characterized as a quick method.

## REFERENCES

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Received November 12, 1954.