Coulometric-potentiometric determination of autoprotolysis constant and relative acidity scale of water

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Abstract: The autoprotolysis constant and relative acidity scale of water were determined by applying the coulometric-potentiometric method and a hydrogen/palladium (H2/Pd) generator anode. In the described procedure for the evaluation of autoprotolysis constant, a strong base generated coulometrically at the platinum cathode in situ in the electrolytic cell, in presence of sodium perchlorate as the supporting electrolyte, is titrated with hydrogen ions obtained by the anodic oxidation of hydrogen dissolved in palladium electrode. The titration was carried out with a glass–SCE electrode pair at 25.0±0.1 °C. The value obtained pKw = 13.91 ± 0.06 is in agreement with literature data. The range of acidity scale of water is determined from the difference between the half-neutralization potentials of electrogenerated perchloric acid and that of sodium hydroxide in a sodium perchlorate medium. The half-neutralization potentials were measured using both a glass-SCE and a (H2/Pd)ind–SCE electrode pairs. A wider range of relative acidity scale of water was obtained with the glass–SCE electrode pair.

Keywords: coulometry; potentiometry; autoprotolysis constant; relative acidity scale; hydrogen-palladium electrode.

INTRODUCTION

A variety of procedures have been used for the evaluation of autoprotolysis constants, mainly based on potentiometric titrations.1 Classical potentiometric procedure for the determination of an autoprotolysis constant requires preparation of standard solutions of strong acid and strong base in the solvent investigated; the parameters such as concentrations of the solutions, and the presence of either acidic or basic impurities, must be accurately evaluated. The determination of the autoprotolysis constant potentiometrically was simplified by generating acid or base coulometrically.

Glab and Hulanicki2 were the first to apply coulometric titrations for the determination of autoprotolytic constants. The values of pKs of solvents were calculated from the potentials measured during the course of a titration of a strong acid ( perchloric acid) with a cathodically generated base. In the described procedure, only one solution containing the acid and the conducting electrolyte has to be prepared, and its concentration is determined from the coulometric alkalimetric titration curve, assuming 100% current efficiency for the generation of the base. The same authors3,4 applied the coulometric titration technique for the determination of the protonation constants of acids and bases in water and non-aqueous solvents.
In previously published papers,\textsuperscript{5,6} it was shown that the use of a standard perchloric acid solution for titration of bases in aqueous and non-aqueous media can be avoided by generating perchloric acid coulometrically at a H$_2$/Pd generator anode. Furthermore, a H$_2$/Pd anode was applied as the source of hydrogen ions in the coulometric determination of the dissociation constant of bases in some aprotic solvents, as well as in the determination of autoprotolysis constants and relative acidity scales of some non-aqueous solvents.\textsuperscript{6,7} In the present study, a H$_2$/Pd generator electrode has been used for the coulometric-potentiometric determination of the autoprotolysis constant of water as well as for the evaluation of relative acidity scale of water.

**EXPERIMENTAL**

**Apparatus**

The apparatus and the electrodes used in this work were described previously.\textsuperscript{7}

**Reagents**

- **Water**: twice distilled. **Sodium perchlorate**: analytical grade. A 0.1 M aqueous sodium perchlorate solution was used as the supporting electrolyte solution.
- **Tris(hydroxymethyl)aminomethane (THAM)**. Analytical grade. THAM was used to prepare a primary standard solution (0.0676 M).

**Procedures**

**Determination of the autoprotolysis constant.** The supporting electrolyte was poured into both the generating (35.0 mL) and the auxiliary (10.0 mL) compartment of the coulometric cell. For the generation of the base both electrodes in the generating circuit were made of platinum; the surface of the generating cathode was about 2 cm$^2$. Base was generated by passing a constant current of 15 mA to give a concentration of 0.006 M. The generator H$_2$/Pd anode and electrode pair glass–SCE were then placed in the generating compartment. Titration of the base was performed with hydrogen ions generated at the H$_2$/Pd anode, at a current of 15 mA. The total concentration of the generated acid was equal to the double initial concentration of the titrated base. Possible interferences due to the diffusion of the solution through the porous diaphragms, separating the anode from the cathode compartment, were avoided by occasional replacement of the catholyte with fresh supporting electrolyte solution. The titration end-point (EP) was determined by the Gran method, which was modified for the coulometric titration. The slope of the glass electrode was 59 mV.

**Determination of the relative acidity scale.** The range of the relative acidity scale of water (mV) was determined from the difference in the half-neutralization potentials during the reaction of perchloric acid with sodium hydroxide, generated coulometrically in the aqueous solution of sodium perchlorate.

\textbf{a)} **Determination of the half-neutralization potential of acid:** The supporting electrolyte solution was poured into the anode (35.0 mL) and cathode (10.0 mL) compartment of the coulometric cell. The (H$_2$/Pd)$_{gen}$ anode and the Pt-cathode were immersed into the anolyte and the catholyte, respectively. The perchloric acid was generated using a current strength of 15 mA, until the concentration of 0.007 M was achieved. The Pt-electrode and the glass-SCE (or a (H$_2$/Pd)$_{ind}$–SCE) pair was then immersed in the anolyte, and the acid was titrated with catholically generated base. The half-neutralization potentials of acid were determined graphically (Fig. 1).

\textbf{b)} **Determination of the half-neutralization potential of base:** The supporting electrolyte solution was poured into the generating (35.0 mL) and the auxiliary (10.0 mL) compartment of the coulometric cell. The base was generated at the Pt-cathode with the current strength of 15 mA, until the concentration of 0.007 M was achieved, and then titrated with the acid generated at the H$_2$/Pd anode. The potentials were measured by means a glass–SCE or a (H$_2$/Pd)$_{ind}$–SCE electrode pair. The half-neutralization potential of base was also determined graphically.

All measurements were carried out at 25.0±0.1 °C in solutions stirred with a magnetic stirrer.

**Coulometric-potentiometric titration of THAM in water.** A THAM solution (2.00 mL) and the sodium perchlorate solution (18.0 mL) were put into the anode compartment of the coulometric cell, and the sodium perchlorate solution (5.0 mL) was poured into the
cathode compartment. The auxiliary electrode (a Pt-wire) was immersed in the catholyte. The \((H_2/Pd)_{\text{gen}}\) anode and the electrode pair glass–SCE or \((H_2/Pd)_{\text{ind}}–\text{SCE}\) were placed in the anolyte. The titration of base was performed with hydrogen ions generated discontinuously at the \(H_2/Pd\) anode, under continuous registration of the potential.

RESULTS AND DISCUSSION

The autoprotolysis constant of water was determined by the coulometric procedure in which strong base was firstly generated cathodically in the electrolytic cell and then titrated by hydrogen ions generated by anodic oxidation of hydrogen dissolved in palladium, in an aqueous sodium perchlorate solution. The concentration of the base is determined from the coulometric acidimetric titration curve, assuming 100 % current efficiency for generation of hydrogen ions at a \((H_2/Pd)_{\text{gen}}\) anode. The changes in hydrogen ion concentration were followed with a glass electrode. For calibration of glass electrode the so-called „\(E^0\)-titration” was used; at a constant ionic strength, the \(e.m.f.\) of the cell is a linear function of the logarithm of hydrogen ion concentration.

The experimental data obtained in the course of coulometric-potentiometric titration of electrogenerated base with perchloric acid generated at a \((H_2/Pd)_{\text{gen}}\) anode at a given ionic strength (0.1 M) were used to calculate the autoprotolysis constant of water. The concentration constant of water autoprotolysis \((pK_w^c = -\log K_w^c)\) was calculated by means of the expression:

\[
pK_w^c = \frac{E_b^0 - E_a^0}{59.16}
\]

were the potentials \(E_b^0\) and \(E_a^0\) represent the specific cell constants for the basic and acid regions, respectively, involving the standard potential of the glass electrode, the potential of the reference electrode, the diffusion potential and the activity factors. The values \(E_b^0\) (mV) and \(E_a^0\) (mV) were calculated from a definite number of points along the titration curve before and after the equivalence point, respectively, from equations:

\[
E_b^0 = E - 59.16 \log \frac{Q_{EP} - Q}{FV}
\]

\[
E_a^0 = E + 59.16 \log \frac{Q - Q_{EP}}{FV}
\]

where \(Q_{EP}\) (C) denotes the amount of charge generated up to the end point of titration of the base, \(Q\) (C) is the quantity of the charge generated up to the measured potential \(E\) (mV), \(V\) is the solution volume (mL) and \(F\) is the Faraday constant (96500 C). The constancy of \(E_b^0\) and \(E_a^0\) over the whole range indicates proper functioning of the indicator electrode and the absence of systematic errors. The detailed record for this procedure is given in Table I.

**TABLE I.**

The concentration constant was recalculated to obtain the thermodynamic value

\[
pK_w = pK_w^c - \log f_+ f_-
\]

by using the known ionic strength (in 0.10 M ionic strength, \(f_+ = 0.83\) and \(f_- = 0.76\)).

The \(pK_w\) values determined coulometrically using a \(H_2/Pd\) anode, as well as the literature data, are listed in Table II. The \(pK_w\) value obtained
experimentally in this study agrees well with the literature data.\textsuperscript{10} This indicates that the procedure proposed here delivers fair results, but that special attention must be paid to avoid the diffusion of the solution through the porous separator.

**TABLE II.**

*The relative acidity scale*

The relative acidity scale ($E_s$) of a solvent defines the approximate potential range which can be used for potentiometric acid–base titrations in the given solvent under the determined experimental conditions. The value of the practical $E_s$ scale can be determined from the difference between the half-neutralization potentials of strong acid and strong base in the applied solvent.\textsuperscript{11}

The relative acidity scale of water was determined in this study coulometrically, from the difference between the half-neutralization potentials of solutions of perchloric acid and sodium hydroxide.

\[
E_s = E_{1/2(\text{HClO}_4)} - E_{1/2(\text{NaOH})}
\]

The half-neutralization potentials of acid were determined graphically from the experimental data obtained in the course of titration of electrogenerated perchloric acid with the coulometrically generated base in sodium perchlorate media (Fig. 1). The potentials were measured using both a glass–SCE and a (H$_2$/Pd)$_{\text{ind}}$–SCE electrode pairs at 25.0±0.1 °C. The half-neutralization potentials of base were also determined graphically, from the experimental data obtained in the course of titration of coulometrically generated sodium hydroxide with perchloric acid generated at an (H$_2$/Pd)$_{\text{gen}}$ anode in an aqueous solution of sodium perchlorate.

The ranges of the relative acidity scale of water, obtained by the coulometric-potentiometric procedure using a (H$_2$/Pd)$_{\text{gen}}$ electrode, as well as the literature data, are summarized in Table III.

**TABLE III.**

The experimentally determined $E_s$ values of acidity scale of water obtained in this study by coulometry differ from the ones obtained by classic potentiometric method.\textsuperscript{11} This difference can be explained by differences in the experimental conditions (titrant, electrode pair, ionic strength, \textit{etc.}) in the present work in comparison to those applied by other authors.

As can be seen (Table III), a wider $E_s$ scale of water is obtained when a glass–SCE electrode pair is used to measure the half-neutralization potentials. This significant difference between the values of $E_s$ scales obtained with a glass–SCE and a (H$_2$/Pd)$_{\text{ind}}$–SCE electrode pairs is caused probably by the lower sensitivity of the (H$_2$/Pd)$_{\text{ind}}$ electrode compared with the glass electrode. Previously, it was shown that the slopes of the potential response of the (H$_2$/Pd)$_{\text{ind}}$ electrode in aqueous media were sub-Nernstian.\textsuperscript{12} Based on this fact, it could be expected that the highest potential jumps at the end-point would be obtained if a glass electrode were used as an indicator electrode.

**Fig. 2.**

Thus, for example, in the coulometric titration of THAM in aqueous media (Fig. 2), the potential jumps at the end-point were, respectively, about 140 and 70 mV when a glass and a (H$_2$/Pd)$_{\text{ind}}$ electrode were used, (for a base concentration 0.007 M). Hence, a relative acidity scale of water determined by coulometry may be a practical and useful criterion for the choice of the optimal conditions (for example, the choice of the favorable
electrode pair) in coulometric-potentio-metric acid-base titration in this solvent.

CONCLUSIONS

The autoprotolysis constant and relative acidity scale of water were determined by applying the coulometric-potentiometric method and a hydrogen/palladium generator electrode. Employing a hydrogen/palladium anode as the source of hydrogen ions, the preparation of a standard solution of acid is avoided and the titrated volume and the ionic strength remain unchanged. This procedure is more rapid and simpler than the classical potentiometric procedure.

Acknowledgement. The authors are grateful to the Ministry of Science and Technological Development of the Republic of Serbia for financial support (Project No. 142060).

REFERENCES

TABLE I. Coulometric determination of the autoprotolysis constant of water; the base in 35 mL cell was generated at a Pt-cathode and then titrated with electrogeneatedacid by the use of an (H_2/Pd)_gen anode; current 15 mA; equivalence point for acid generation corresponds to $Q_{EP} = 19310 \text{ mC}$; supporting electrolyte 0.1 M sodium perchlorate.

<table>
<thead>
<tr>
<th>Charge ($Q$)/C</th>
<th>e.m.f ($E$)/mV</th>
<th>$E_b^0$ /mV</th>
<th>$E_a^0$ /mV</th>
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<tr>
<td>1.80</td>
<td>322</td>
<td>457.4</td>
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<td>2.70</td>
<td>321</td>
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<td>3.60</td>
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<td>4.50</td>
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<td>457.7</td>
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<td>5.40</td>
<td>317</td>
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<td>11.70</td>
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<tr>
<td>35.10</td>
<td>−214</td>
<td>−351.6</td>
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</tr>
<tr>
<td>36.00</td>
<td>−215</td>
<td>−351.2</td>
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</table>

Average 459.6  −351.0

\[ pK_w^c = \frac{459.6 - (-351.4)}{59.16} = 13.70; \quad pK_w = 13.89 \]
### TABLE II. Autoprotolysis constant of water obtained by coulometry at 25.0±0.1 °C

<table>
<thead>
<tr>
<th>pK(_w) ± SD(^a)</th>
<th>pK(_w) ± SD(^a)</th>
<th>pK(_w) literature data(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.71±0.06</td>
<td>13.91±0.06</td>
<td>14.0</td>
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</table>

\(^a\)Standard deviation; number of determinations: 6

\(^b\)
TABLE III. The relative acidity scale of water obtained by coulometry at 25.0±0.1 °C; supporting electrolyte 0.10 M sodium perchlorate

<table>
<thead>
<tr>
<th>Electrode pair</th>
<th>$E_{1/2}(\text{acid})\pm SD$ /mV</th>
<th>$E_{1/2}(\text{base})\pm SD$ /mV</th>
<th>$E_s\pm SD$ /mV</th>
<th>$E_s$ /mV</th>
<th>literature data$^{11}$</th>
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</thead>
<tbody>
<tr>
<td>Glass-SCE</td>
<td>$-79\pm 3$</td>
<td>411±7</td>
<td>490±6</td>
<td>540</td>
<td></td>
</tr>
<tr>
<td>(H$<em>2$/Pd)$</em>{\text{ind}}$-SCE</td>
<td>66±4</td>
<td>276±14</td>
<td>210±9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Standard deviation; number of determinations: 4
FIGURE CAPTIONS

Fig. 1. The dependence of the potential of the cell on log [HA/(100 – HA)], where HA represent percent of neutralized acid. The graphical determination of half-neutralization potential of perchloric acid is illustrated.

Fig. 2. Coulometric-potentiometric titration curves of tris(hydroxymethyl)aminomethane in aqueous media.
$E_i/mV$

$\log\left[ \frac{HA}{(100-HA)} \right]$

Fig. 1.
Fig. 2.