Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 75 (11) 1575–1582 (2010)
JSCS–4722

UDC 628.1.033:543.551+543.554:
544.362.2:544.6.076.32–43
Original scientific paper

Coulometric–potentiometric determination of the autoprotolysis constant and the relative acidity scale of water

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(Received 16 March, revised 6 July 2010)

Abstract: The autoprotolysis constant and the relative acidity scale of water were determined by applying the coulometric–potentiometric method and a hydrogen/palladium (H_2/Pd) generator anode. In the described procedure for the evaluation of the autoprotolysis constant, a strong base, coulometrically generated *in situ* at the platinum cathode in the electrolytic cell, in the presence of sodium perchlorate as the supporting electrolyte, was titrated with hydrogen ions obtained by the anodic oxidation of hydrogen dissolved in the palladium electrode. The titration was performed with a glass–SCE electrode pair at 25.0±0.1 °C. The obtained value, $pK_w = 13.91\pm0.06$, is in agreement with literature data. The range of the acidity scale of water was determined from the difference between the half-neutralization potentials of the 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 $(H_2/Pd)_{ind}$–SCE electrode pair. A wider range of the 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] The classical potentiometric procedure for the determination of an autoprotolysis constant requires the preparation of standard solutions of strong acids and strong bases in the investigated solvent; the parameters, such as concentrations of the solutions and the presence of either acidic or basic impurities, must be accurately evaluated. The potentio-

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doi: 10.2298/JSC100316094D

metric determination of autoprotolysis constants was simplified by generating the acid or base coulometrically.

Glab and Hulanicki[2] were the first to apply coulometric titrations for the determination of autoprotolytic constants. The values of pK_S 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 had to be prepared, and its concentration was determined from the coulometric alkalimetric titration curve, assuming 100 % current efficiency for the generation of the base. The same authors[3,4] 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,[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.[6,7] In the present study, a H_2/Pd generator electrode was 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.[7]

Reagents

Water, twice distilled. Sodium perchlorate, analytical grade. A 0.10 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 the 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 double the 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 an aqueous solution of sodium perchlorate.

a) Determination of the half-neutralization potential of an 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 a 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 cathodically generated base. The half-neutralization potentials of acid were determined graphically (Fig. 1).

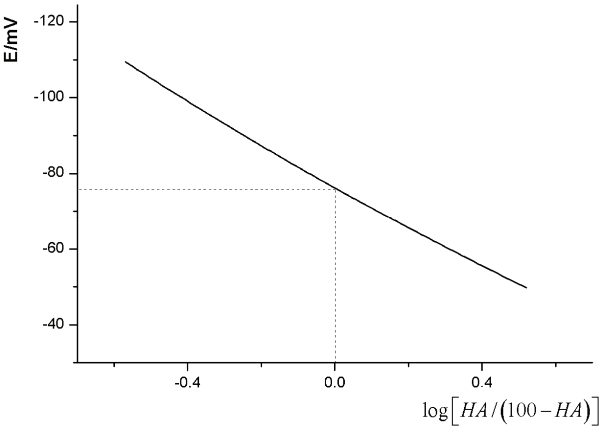

Fig. 1. The dependence of the potential of the cell on log [*HA*/(100 – *HA*)], where *HA* represent the percent of neutralized acid. The graphical determination of the half-neutralization potential of perchloric acid is illustrated.

b) Determination of the half-neutralization potential of a 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 a 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 the 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 $(H_2/Pd)_{gen}$ anode and the electrode pair glass–SCE or $(H_2/Pd)_{ind}$–SCE were placed in the anolyte. The titration of the base was performed with hydrogen ions generated discontinually 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 a strong base was first generated cathodically in the electrolytic cell and then titrated with hydrogen ions generated by the anodic oxidation of hydrogen dissolved in palladium, in an aqueous sodium perchlorate solution. The concentration of the base was determined from the coulometric acidimetric titration curve, assuming 100 % current efficiency for the generation of hydrogen ions at the $(H_2/Pd)_{gen}$ anode. The changes in hydrogen ion concentration were followed with a glass electrode. For calibration of glass electrode the so-called "E^0-titration"[8] 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 the coulometric–potentiometric titration of the electrogenerated base with perchloric acid generated at a $(H_2/Pd)_{gen}$ anode at a given ionic strength (0.10 M) were used to calculate the autoprotolysis constant of water. The concentration constant of water autoprotolysis ($\mathrm{p}K_\mathrm{w}^\mathrm{c} = -\log K_\mathrm{w}^\mathrm{c}$) was calculated by means of the expression:

$$\mathrm{p}K_\mathrm{w}^\mathrm{c} = \frac{E_\mathrm{b}^0 - E_\mathrm{a}^0}{59.16}$$

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, using the equations:

$$E_\mathrm{b}^0 = E - 59.16\ \log \frac{Q_\mathrm{EP} - Q}{FV}$$

$$E_\mathrm{a}^0 = E + 59.16\ \log \frac{Q - Q_\mathrm{EP}}{FV}$$

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 mol^{-1}). The constancy of E_b^0 and E_a^0 over the whole range indicates the proper functioning of the indicator electrode and the absence of systematic errors. The detailed record for this procedure is given in Table I.

The concentration constant was recalculated to obtain the thermodynamic value:

$$\mathrm{p}K_\mathrm{w} = \mathrm{p}K_\mathrm{w}^\mathrm{c} - \log f_+ f_-$$

by using the known ionic strength (in 0.10 M ionic strength, $f_+ = 0.83$ and $f_- = 0.76$).[9]

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 electrogenerated acid by the use of an $(H_2/Pd)_{gen}$ anode; current 15 mA; equivalence point for acid generation corresponds to Q_{EP} = 19310 mC; the supporting electrolyte was 0.10 M sodium perchlorate;

$$\mathrm{p}K_\mathrm{w}^\mathrm{c} = \frac{459.6-(-351.0)}{59.16} = 13.70\,;\ \mathrm{p}K_\mathrm{w} = 13.89$$

Q / C	E / mV	E_b^0 / mV	E_a^0 / mV
1.80	322	457.4	–
2.70	321	457.8	–
3.60	319	457.2	–
4.50	318	457.7	–
5.40	317	458.4	–
6.30	317	460.1	–
7.20	316	460.9	–
8.10	314	461.0	–
9.00	312	461.1	–
9.90	311	462.5	–
10.80	307	461.2	–
11.70	305	462.0	–
12.60	300	458.4	–
13.50	295	459.2	–
24.30	–183	–	–352.5
25.20	–188	–	–350.6
26.10	–192	–	–351.0
27.00	–195	–	–350.9
27.90	–198	–	–351.1
28.80	–200	–	–350.6
29.70	–202	–	–350.3
30.60	–204	–	–350.2
31.50	–206	–	–350.2
32.40	–208	–	–351.4
33.30	–210	–	–350.7
34.20	–212	–	–351.1
35.10	–214	–	–351.6
36.00	–215	–	–351.2
Average	–	459.6	–351.0

The pK_w values determined coulometrically using a H_2/Pd anode, as well as the literature date, are listed in Table II. The pK_w value obtained experimentally in this study agrees well with the literature data.[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. Autoprotolysis constant of water obtained by coulometry at 25.0±0.1 °C

pK_w^c ±SD^a	pK_w±SD^a	pK_w Literature data[10]
13.71±0.06	13.91±0.06	14.0

[a] Standard deviation, number of determinations: 6

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 a strong acid and a strong base in the applied solvent.[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.

$$E_S = E_{1/2(HClO_4)} - E_{1/2(NaOH)}$$

The half-neutralization potentials of the acid were determined graphically from the experimental data obtained in the course of the 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 $(H_2/Pd)_{ind}$–SCE electrode pairs at 25.0±0.1 °C. The half-neutralization potentials of the base were also determined graphically, from the experimental data obtained in the course of the titration of coulometrically generated sodium hydroxide with perchloric acid generated at an $(H_2/Pd)_{gen}$ 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 $(H_2/Pd)_{gen}$ electrode, as well as literature data, are summarized in Table III.

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

Electrode pair	$E_{1/2}$(acid)±*SD*[a] mV	$E_{1/2}$(base)±*SD* mV	E_S±*SD* mV	E_S / mV (literature data[11])
Glass–SCE	–79±3	411±7	490±6	540
$(H_2/Pd)_{ind}$–SCE	66±4	276±14	210±9	–

[a] Standard deviation, number of determinations: 4

The experimentally determined E_S values of the acidity scale of water obtained in this study by coulometry differ from the ones obtained by the classic potentiometric method.[11] This difference can be explained by differences in the experimental conditions (titrant, electrode pair, ionic strength, *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 was obtained when a glass–SCE electrode pair was used to measure the half-neutralization potentials. This significant difference between the values of E_S scales obtained with a glass–SCE and a $(H_2/Pd)_{ind}$–SCE electrode pairs is probably caused by the lower sensitivity of the $(H_2/Pd)_{ind}$ electrode compared with the glass electrode. Previously, it was shown that the slopes of the potential response of the $(H_2/Pd)_{ind}$ electrode in aqueous media were sub-Nernstian.[12] Based on this fact, it could expected that the highest potential jumps at the end-point would be obtained if a glass electrode were used as an indicator electrode.

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 $(H_2/Pd)_{ind}$ electrode were used, (for a base concentration 0.0070 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 a favorable electrode pair) in coulometric-potentiometric acid–base titration in this solvent.

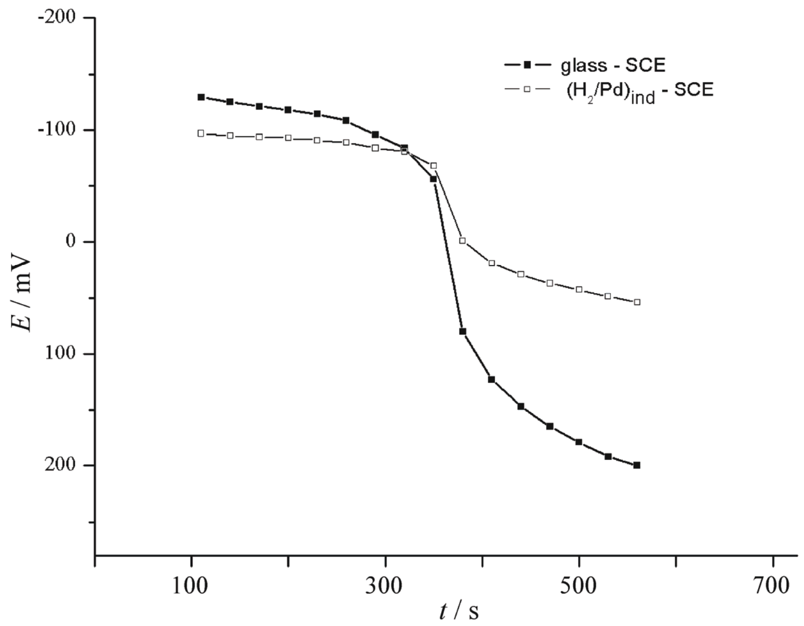

Fig. 2. Coulometric–potentiometric titration curves of tris(hydroxymethyl)aminomethane in aqueous media.

CONCLUSIONS

The autoprotolysis constant and relative acidity scale of water were determined by applying the coulometric–potentiometric method and a hydrogen/palladium generator electrode. By employing a hydrogen/palladium anode as the source of hydrogen ions, the preparation of a standard solution of acid was avoided and the titrated volume and the ionic strength remained 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).

ИЗВОД

КУЛОМЕТРИЈСКО–ПОТЕНЦИОМЕТРИЈСКО ОДРЕЂИВАЊЕ КОНСТАНТЕ АУТОПРОТОЛИЗЕ И РЕЛАТИВНЕ СКАЛЕ КИСЕЛОСТИ ВОДЕ

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Константа аутопротолизе и релативна скала киселости воде одређене су применом кулометријско–потенциометријске методе и водоник/паладијумове (H_2/Pd) генераторске аноде. У приказаном поступку за одређивање константе аутопротолизе воде, јака база генерисана *in situ* кулометријски на Pt-катоди, у раствору натријум-перхлората као електролита, титрисана је водониковим јонима добијеним анодном оксидацијом водоника раствореног у паладијуму. Титрација је извођена применом електродног пара стаклена електрода–ЗКЕ на 25,0±0,1 °C. Добијена вредност pK_w = 13,91±0,06 је у сагласности са литературним подацима. Релативна киселинска скала воде одређена је из разлике полу-неутрализационих потенцијала раствора електрогенерисане перхлорне киселине и натријум-хидроксида у натријум-перхлоратној средини. За мерење полу-неутрализационих потенцијала коришћени су електродни парови стаклена електрода–ЗКЕ и (H_2/Pd)$_{инд}$–ЗКЕ. Применом електродног пара стаклена електрода–ЗКЕ добијене су веће вредности за релативну скалу киселости воде.

(Примљено 16. марта, ревидирано 6. јула 2010)

REFERENCES

1. A. Albert, E. P. Serjeant, *The Determination of Ionization Constants*, Chapman Hall, London, 1971
2. S. Glab, A. Hulanicki, *Talanta* **28** (1981) 183
3. S. Glab, E. Skrzydlewska, A. Hulanicki, *Talanta* **37** (1987) 411
4. S. Glab, U. Nowicka, *Mikrochim. Acta* **2** (1987) 229
5. R. P. Mihajlović, V. J. Vajgand, Lj. N. Jakšić, *Talanta* **38** (1991) 333
6. R. P. Mihajlović, Lj. N. Jakšić, R. M. Džudović, *Anal. Chim. Acta* **557** (2006) 37 (and references therein)
7. R. M. Džudović, Lj. N. Jakšić, *J. Serb. Chem. Soc.* **73** (2008) 871
8. A. Johansson, S. Johansson, *Analyst*, **103** (1978) 305
9. J. Kielland, *J. Am. Chem. Soc.* **59** (1937) 1675
10. R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, 2nd ed., Butterworths, London, 1968, p. 230
11. A. P. Kreshkov, Analytical Chemistry of Non-Aqueous Solutions, Khimiya, Moscow, 1982, p. 183 (in Russian)
12. Lj. N. Jakšić, R. M. Džudović, R. P. Mihajlović, *J. Serb. Chem. Soc.***70** (2005) 243.