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Determination of relative acidity scales for some dipolar aprotic solvents by coulometry using a hydrogen–palladium electrode

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Abstract: A coulometric–potentiometric procedure for the determination of relative acidity scales of acetone, methylethyl ketone, methyl-isobutyl ketone and propylene carbonate is described. The range of the relative acidity scale of a solvent was determined from the difference between the half-neutralization potential of perchloric acid and that of tetrabutylammonium hydroxide. The perchloric acid was generated *in situ* from a hydrogen–palladium electrode in presence of sodium perchlorate or tetrabutylammonium perchlorate as the supporting electrolyte. The electrode pairs glass–SCE and (H₂/Pd)_{ind}–SCE were applied for the measurement of the half-neutralization potentials of the acid and base. A wider range of relative acidity scale of the solvents was obtained with the glass–SCE electrode pair and tetrabutylammonium perchlorate as the supporting electrolyte.

Keywords: relative acidity scale; coulometric generation of perchloric acid; hydrogen–palladium electrode; non-aqueous solvents.

INTRODUCTION

The choice of solvent as the medium for acid–base titrations was done on the basis of the thermodynamic constants of the solvent, the dissociation constant of the titrated acid (base), the half-neutralization potential of the titrated acid (base) in the investigated solvent and the relative acidity scale of the solvent.¹

The autoprotolysis constant, K_s , is one of the basic thermodynamic constants of a solvent, which depends on numerous parameters including the acidity and basicity of the solvent, the relative permeability and polarity of the solvent molecules, *etc.* The K_s value gives information directly relevant to the extent of the acidity scale, pK_s . Solvents with higher pK_s values have a stronger differentiating effect during the titration of multicomponent electrolyte mixtures.

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The relative acidity scale of a solvent, E_s , has no physical meaning as does the acidity scale pK_s , which is calculated from the autoprotolysis constant of the solvent. The value of the E_s scale of a solvent is calculated from the difference between the half-neutralization potentials of a strong acid and a strong base in the given solvent. The relative acidity scale defines for every solvent the approximate potential ranges which can be used for potentiometric acid–base titrations under the determined experimental conditions (titrant, electrode pair, *etc.*). Hence, the E_s scale is a practical criterion for the choice of the optimal conditions in potentiometric acid–base titrations in the given solvent. With increasing range of the E_s scale, the possibility of the titration of weak bases (acids) and of differentiating titrations of multicomponent mixtures of bases (acids) in the solvent is increased.

There are a few data in literature concerning the relative acidity scale of non-aqueous solvents.^{2–6} The presented procedures for the evaluation of the E_s scale were based on the determination the difference between the half-neutralization potentials of perchloric acid and tetraethylammonium hydroxide (TEAH) or tetrabutylammonium hydroxide (TBAH) in the given solvent. It was found that the range of the scale depends on the nature of the solvent, the type of the electrode, the nature and concentration of the titrant and the presence of water and other impurities in the solvent.

Although perchloric acid is a strong electrolyte in most non-aqueous solvents, its application as a titrant is connected with some experimental difficulties, such as the instability of the acid in organic solvents, the presence of water, *etc.* It might be expected that an improvement of the procedure of classical titrations with perchloric acid would be obtained by using coulometric titration. With the coulometric titration technique, it is not necessary to prepare a titrant solution as this is generated electrolytically. It was shown⁷ that many organic compounds (phenols, thiols, ascorbic acid, esters of gallic acid, *etc.*) and mercury, as well as hydrogen (or deuterium) dissolved in palladium can be successfully applied as anodic depolarizers for the coulometric generation of acids in non-aqueous solvents. The most favorable anodic depolarizer for the coulometric titration of bases as well as for the coulometric determination of protonation constants in non-aqueous solvents is hydrogen dissolved in palladium. The anodic oxidation of hydrogen generates “dry” hydrogen ions, by which means the introduction of a titrant into the solution is avoided, the titrated volume and the ionic strength remain unchanged and the procedure is simplified.

No data have been reported on the application of coulometric titrant generation for determination of the relative acidity scale of solvents.

Employing the possibility of the direct H^+ generation by the electrooxidation of hydrogen dissolved in palladium, in this work a procedure for the coulometric–

—potentiometric determination of the relative acidity scales of some dipolar aprotic solvents was developed.

EXPERIMENTAL

Reagents

All employed chemicals were of analytical grade from Merck or Fluka. Prior to use, acetone (AC), methylethyl ketone (MEK) and methyl-isobutyl ketone (MIBK) were purified by procedures described in the literature.⁸ Propylene carbonate (PC) was used without further purification.

Tetrabutylammonium hydroxide (TBAH) in a 2-propanol–methanol mixture (0.10 M) was used. The exact concentration of TBAH was determined coulometrically using a hydrogen–palladium generator electrode.

The liquid organic bases were first dried over fused potassium hydroxide and then distilled under reduced pressure. The concentration of the solutions of the bases were controlled by titrating them with H^+ generated by the oxidation of hydrogen dissolved in palladium.

The supporting electrolyte was 0.10 M sodium perchlorate or 0.10 M tetrabutylammonium perchlorate (TBAP) in the required solvent.

Apparatus

The apparatus for the coulometric–potentiometric determination of relative acidity scales of the solvents is shown in Fig. 1.

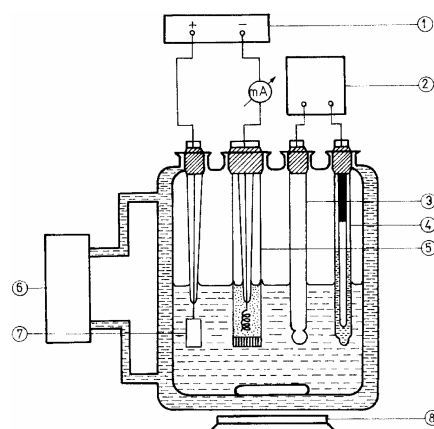


Fig. 1. Schematic diagram of the apparatus for the coulometric–potentiometric determination of the relative acidity scale of solvents: (1) current stabilizer, (2) pH-meter, (3) glass electrode, (4) calomel electrode, (5) Pt-cathode, (6) thermostat, (7) H_2/Pd electrode and (8) magnetic stirrer.

The current source was a voltage–current stabilizer (type STNS, Vinča, Belgrade). The current in the generating circuit was measured with a precise milliamperimeter (Iskra, Kranj). The anode and cathode compartments of the electrolytic vessel were separated by a sintered glass disk of porosity 4; the volume of anolyte was 40 ml, and that of the catholyte 10 ml. The potential was measured by means of a pH-meter Radiometer pHM-26. The temperature of the solution was kept constant by circulating thermostated water through the outer glass-mantle of the vessel. The solution was continuously stirred with a magnetic stirrer.

Electrodes

The generator electrode, $(H_2/Pd)_{gen}$, was a palladium plate (1 cm×2 cm×0.5 cm), saturated with hydrogen obtained by electrolyzing a dilute aqueous sulfuric acid solution.

The indicator electrode, $(\text{H}_2/\text{Pd})_{\text{ind}}$, was made in the form of a palladium spiral wire sealed into a glass tube by means of a platinum wire. The electrode had previously been saturated with hydrogen obtained by the electrolysis of water. The response of $(\text{H}_2/\text{Pd})_{\text{ind}}$ electrode in the solvents was investigated from the potential measurements in solutions of coulometrically generated perchloric acid (within the concentration range 0.010 M to 0.0010 M) in sodium perchlorate media. It was found (Fig. 2) that the potential of the $(\text{H}_2/\text{Pd})_{\text{ind}}$ electrode showed a sub-Nernstian dependence on the logarithm of the concentration of perchloric acid, with a slope of 46 mV in acetone and 44 mV in methylethyl ketone.

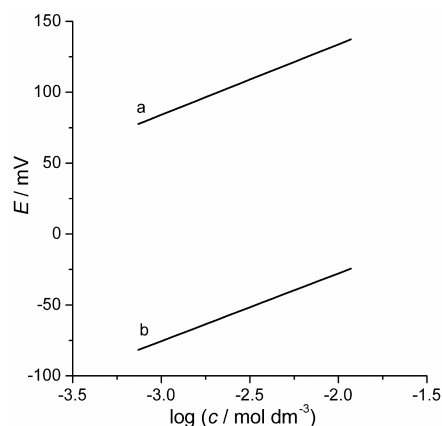


Fig. 2. Plot of the potential of the $(\text{H}_2/\text{Pd})_{\text{ind}}$ electrode vs. logarithm of the concentration of the electrogenerated perchloric acid in (a) acetone and (b) methylethyl ketone.

A glass electrode, type G-202B (Radiometer, Copenhagen), was used. The electrode was conditioned in the required solvent before use.

A modified saturated calomel electrode, type K201 (Radiometer, Copenhagen), with potassium chloride in methanol was used as the reference electrode.

Procedures

Determination of the relative acidity scale. The relative acidity scale of AC, MEK, MIBK and PC were determined from the difference in the half-neutralization potentials of perchloric acid and TBAH. Two electrode pairs, a glass-SCE and a $(\text{H}_2/\text{Pd})_{\text{ind}}$ -SCE, were used for the measurement of the half-neutralization potentials of the acid and base.

Determination of the potential of the half-neutralization of perchloric acid. The supporting electrolyte (sodium perchlorate or TBAP) was poured into the anode (40 ml) and cathode (10 ml) compartments of the electrolytic vessel. The platinum and $(\text{H}_2/\text{Pd})_{\text{gen}}$ electrodes were immersed into the catholyte and anolyte, respectively. The required amount of hydrogen ions was generated at the $(\text{H}_2/\text{Pd})_{\text{gen}}$ anode (current of 5.0 mA). The coulometrically obtained perchloric acid was then half-neutralized with a standard solution of TBAH. The potential of half-neutralization of perchloric acid was read 60 min after thermostating (25 °C).

Determination of the potential of half-neutralization of TBAH. The supporting electrolyte was placed into the cathode and anode compartments up to the same level. A suitable volume of a standard solution of TBAH (0.500 ml) was added to the anolyte and then titrated to half neutralization with hydrogen ions generated at the $(\text{H}_2/\text{Pd})_{\text{gen}}$ anode. The half-neutralization potential of the base was also measured after thermostating the solution.

Coulometric-potentiometric titrations of mixtures of bases in propylene carbonate. The supporting electrolyte was poured into the anode (20 ml) and cathode (5.0 ml) compartments of the electrolytic vessel. The platinum wire was dipped into the catholyte and the $(\text{H}_2/\text{Pd})_{\text{gen}}$

electrode and the desired electrode couple (glass–SCE or $(\text{H}_2/\text{Pd})_{\text{ind}}$ –SCE) were placed in the anolyte. A weighed amount of the base being determined was added to the anolyte, the current was switched on; hydrogen ions were generated discontinuously and the potentials were read.

RESULTS AND DISCUSSION

The relative acidity scales of acetone, methylethyl ketone, methyl-isobutyl ketone and propylene carbonate were determined by coulometry from the difference between the half-neutralization potentials of solutions of perchloric acid and TBAH of the same concentration in the investigated solvent.

$$E_s = E_{1/2}(\text{HClO}_4) - E_{1/2}(\text{TBAH})$$

In order to obtain a half-neutralized solution of perchloric acid, the required amount of acid (1.67×10^{-3} M) was generated *in situ* from the $(\text{H}_2/\text{Pd})_{\text{gen}}$ electrode and then neutralized to 50 % with a standard solution of TBAH. A half-neutralized solution of TBAH was obtained by titrating a solution of the base (1.67×10^{-3} M) to 50 % with hydrogen ions coulometrically generated at an $(\text{H}_2/\text{Pd})_{\text{gen}}$ anode. The half-neutralization potentials of perchloric acid and TBAH were measured using both a glass–SCE and a $(\text{H}_2/\text{Pd})_{\text{ind}}$ –SCE electrode pair.

As an example, the calculation of the relative acidity scale of acetone from the experimental data is shown in Table I.

TABLE I. Determination of the relative acidity scale of acetone using a H_2/Pd generator electrode; $c(\text{TBAH}) = 1.67 \times 10^{-3}$ M; $c(\text{HClO}_4) = 1.67 \times 10^{-3}$ M; supporting electrolyte sodium perchlorate (0.10 M); current 5.0 mA

Electrode pair	Number of determinations	$E_{1/2}(\text{HClO}_4)$ / mV	$E_{1/2}(\text{TBAH})$ / mV	E_s / mV	S^a / mV
Glass–SCE	6	-470 ± 4	$+182 \pm 6$	652	9
$(\text{H}_2/\text{Pd})_{\text{ind}}$ –SCE	4	-120 ± 7	-418 ± 3	298	10

^aStandard deviation; the values of the standard deviation represent the accuracy of the measurement of the relative acidity scales of the investigated solvents

The ranges of the relative acidity scales of the investigated solvents, obtained by the coulometric–potentiometric procedure, are shown in Fig. 3.

As can be seen from Fig. 3, various intervals of the relative acidity scale were obtained for one solvent; the range of the E_s scale depended on the electrode pair and the nature of the employed supporting electrolyte. When a glass–SCE electrode pair was used for measuring the half-neutralization potentials, a wider acidity scale of the solvent was obtained than when a $(\text{H}_2/\text{Pd})_{\text{ind}}$ –SCE electrode couple was applied. Thus, for example, the E_s scale of acetone (in a sodium perchlorate medium) determined with a glass–SCE and a $(\text{H}_2/\text{Pd})_{\text{ind}}$ –SCE electrode pair were about 650 and 300 mV, respectively (Table I). This difference in the relative acidity scale of a solvent can be explained by the sensitivity of the $(\text{H}_2/\text{Pd})_{\text{ind}}$ electrode being lower than that of a glass electrode in the investigated solvents; the slopes of the potential response of the $(\text{H}_2/\text{Pd})_{\text{ind}}$ electrode were sub-Nernstian (Fig. 2).

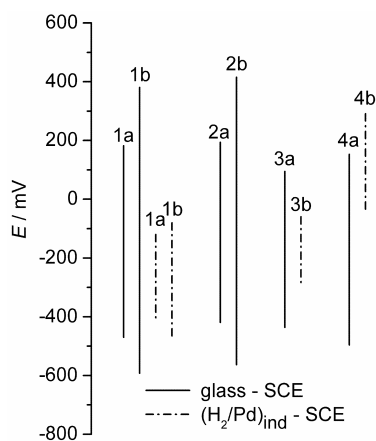


Fig. 3. The relative acidity scale of AC (1), MEK (2), MIBK (3) and PC (4) in (a) sodium perchlorate and (b) TBAP media.

On the basis of this fact, it is to be expected that the highest potential jumps at the end-point would be obtained if a glass electrode were used for the detection of the end-point in the employed solvents. The curves of the coulometric-potentiometric titrations of two-component mixtures of bases in propylene carbonate as the solvent using glass-SCE and $(\text{H}_2/\text{Pd})_{\text{ind}}$ -SCE electrode couples are shown in Fig. 4.

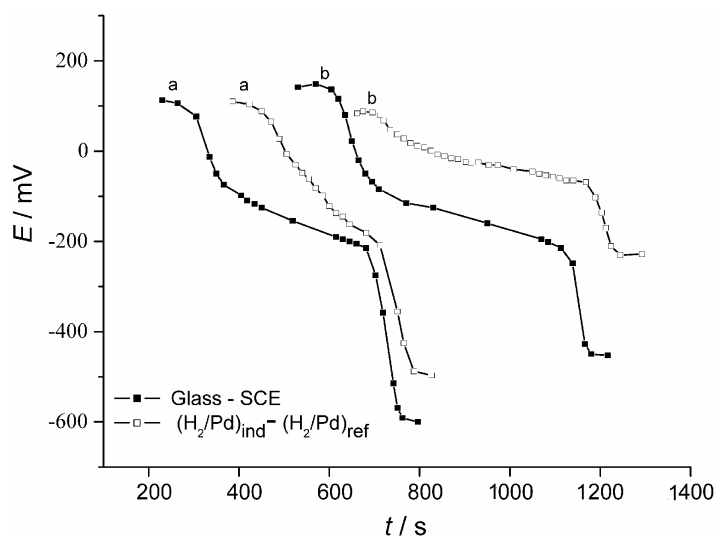


Fig. 4. Coulometric-potentiometric titration curves of mixtures of bases in propylene carbonate: (a) triethylamine + quinoline and (b) triethylamine + 2,2'-bipyridyl.

In the coulometric titration of a mixture of bases, triethylamine + 2,2'-bipyridyl, the potential jumps recorded for the first and second end-point were 60 and 150 mV, respectively, when a glass electrode was used and 30 and 60 mV, respectively, when a $(\text{H}_2/\text{Pd})_{\text{ind}}$ electrode was used. As in PC, in the other dipolar

aprotic solvents (AC, MEK and MIBK) in accordance with their E_s scales, coulometric–potentiometric titrations of mixtures of bases can be successfully performed using a glass indicator electrode.⁹

The range of a relative acidity scale of a solvent depends on the nature of the supporting electrolyte and also on the presence of water. When TBAP was applied as the supporting electrolyte instead sodium perchlorate, wider E_s scales were obtained. The large influence of the supporting electrolyte on the E_s scales determined using a glass electrode can be explained by specific effects of the cation of the supporting salt on the sensitivity of this electrode.

Water lowered the range of the relative acidity scale in all the investigated solvents. It was found that the addition of small amounts of water (less than 1 %) in the anolyte had a large effect on the relative acidity scale of the solvent. Thus, after the addition of 0.30 % water, the relative acidity scale of acetone was narrowed by 65 mV, whereas after the addition of a further 0.70 % water, the scale was narrowed by an additional 60 mV. In accordance with the influence of water on the E_s scale of the solvent, it is to be expected that the potential jumps at the end-point in the coulometric–potentiometric titrations of bases (acids) will be decreased.

CONCLUSIONS

Based on the presented results, it may be concluded that a generator hydrogen–palladium electrode can be applied for the coulometric–potentiometric determination of relative acidity scales of dipolar aprotic solvents. By applying a hydrogen–palladium generator electrode as a source of H^+ , the use of a standard solution of perchloric acid is avoided and the effect of water present in the acid solution is eliminated. A relative acidity scale determined by this method is a practical and useful criterion, which could find application in coulometric–potentiometric acid–base titrimetry in non-aqueous solvents.

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ИЗВОД

КУЛОНОМЕТРИЈСКО ОДРЕЂИВАЊЕ РЕЛАТИВНЕ СКАЛЕ КИСЕЛОСТИ НЕКИХ ДИПОЛАРНИХ АПРОТИЧНИХ РАСТВОРАЧА ПРИМЕНОМ ВОДНИК–ПАЛАДИЈУМОВЕ ЕЛЕКТРОДЕ

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Приказан је поступак за кулонометријско–потенциометријско одређивање релативних скала киселости ацетона, метилетил кетона, метилизобутил кетона и пропилен-карбоната. Вредност релативне скале киселости растварача одређена је из разлике полу-неутрализационих потенцијала перхлорне киселине и тетрабутиламонијум-хидроксида. Перхлорна киселина је генерисана *in situ* на водоник–паладијумовој електроди у присуству натријум-пер-

хлората или тетрабутиламонијум-перхлората као основног електролита. За мерење полу-неутрализационих потенцијала киселине и базе коришћени су електродни парови стаклена-ЗКЕ и $(\text{H}_2/\text{Pd})_{\text{инд}}$ -ЗКЕ. Применом електродног пара стаклена-ЗКЕ и тетрабутиламонијум-перхлоратног основног електролита добијене су веће вредности за релативне скале киселости испитиваних растварача.

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