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*Original scientific paper*

## The application of hydrogen–palladium electrode for potentiometric acid–base determinations in tetrahydrofuran

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**Abstract:** The application of the hydrogen–palladium electrode (H<sub>2</sub>/Pd) as an indicator electrode for the determination of the relative acidity scale ( $E_s$ , mV) of tetrahydrofuran (THF) and potentiometric titrations of acids in this solvent were investigated. The relative acidity scale of THF was determined from the difference between the half-neutralization potentials of perchloric acid and tetrabutylammonium hydroxide (TBAH), which were measured using both H<sub>2</sub>/Pd–SCE and glass–SCE electrode pairs. The experimentally obtained value of the  $E_s$  scale of THF with the H<sub>2</sub>/Pd–SCE electrode pair was 1155 mV, while that obtained with the glass–SCE electrode pair was 880 mV. By using an H<sub>2</sub>/Pd indicator electrode, the individual acids (benzoic acid, palmitic acid, maleic acid, acetyl acetone and  $\alpha$ -naphthol) and two component acid mixtures (benzoic acid +  $\alpha$ -naphthol, palmitic acid +  $\alpha$ -naphthol, maleic acid +  $\alpha$ -naphthol and maleic acid + phthalic acid) were titrated with a standard solution of TBAH. In addition, sodium methylate and potassium hydroxide proved to be very suitable titrating agents for the titrations of the individual acids and the acids in mixtures, respectively. The relative error of the determination of acids in the mixtures was less than 3 %. The results are in agreement with those obtained using a conventional glass electrode. The advantages of the H<sub>2</sub>/Pd electrode over a glass electrode in the potentiometric acid–base determinations in THF lie in the following: this electrode gives a wider relative acidity scale for THF, larger potential jumps at the titration end-point and relatively fast response times. Furthermore, it is very durable, simple to prepare and can be used in the titrations of small volumes.

**Keywords:** relative acidity scale; hydrogen–palladium electrode; potentiometry; acid mixtures; tetrahydrofuran.

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## INTRODUCTION

Tetrahydrofuran (THF) is a dipolar aprotic protophilic solvent with a low relative permittivity ( $\epsilon_r = 7.39$  at 298.15 K), a dipole moment of  $5.4 \times 10^{-30}$  C m and a large acidity scale (34.7 pK<sub>s</sub>). It is a colorless, water-miscible organic liquid with low viscosity (0.48 cP at 25 °C) and a wide liquid range (165 to 339 K).<sup>1</sup> THF is an excellent solvent for dissolving a wide variety of substances, such as ionic species, organometallic compounds and many polymeric materials.<sup>2–4</sup> The solvatochromic properties of THF (hydrogen-bond donor capacity,  $\alpha = 0$ , polarity,  $\pi = 0.58$ , and low hydrogen-bond acceptor capacity,  $\beta = 0.55$ ), and autodissociation constant of the solvent determine the high resolution of acids strength in THF. Based on the dissociation constants of series of acids and their tetrabutylammonium salts in THF, it was shown that the resolution of acid strengths in THF is higher than that in water and methanol and similar to those in acetone, dimethyl sulfoxide and 4-methylpentan-2-one.<sup>5–9</sup>

From analytical point of view, THF is a suitable medium for the titrations of substances exhibiting acidic characteristics in this solvent. Numerous organic compounds, such as alcohols, acetophenones, esters, anilides, carbamates and lactams, can be titrated as very weak acids.<sup>10</sup> The determination of carbamates, lactams and ureas is important since these compounds are often the active ingredients in many pesticides and pharmaceutical chemical. Champion and Bush<sup>4</sup> determined coulometrically the weak acrylic acid content incorporated in a copolymer with electrically generated tetrabutylammonium hydroxide (TBAH) in THF. Meng-Liang and Chang-Yi<sup>11</sup> reported the potentiometric micro-titration of *p*-phthalic acid and Barron and Barbosa<sup>6</sup> performed differential potentiometric titrations of acids in THF medium.

A glass electrode is most frequently used indicator electrode for potentiometric acid–base titrations, both in aqueous and non-aqueous media. However, the potential response of a glass electrode in non-aqueous solutions is often slow; in some cases, one hour is required for the establishment of the equilibrium potential. In addition, the electrode has a limited useful life when employed in non-aqueous titrations because the solvents dehydrate the glass membrane, thereby reducing its response to hydrogen ions. These properties of glass electrodes have led to intensive research of new indicator electrodes for potentiometric acid–base titrations in non-aqueous media. As alternatives to a glass electrode, metal and metalloid indicator electrodes, metallic electrodes coated with layer of hydroxide or oxide and some natural minerals have been employed.<sup>12–21</sup>

Mihajlović *et al.*<sup>22–28</sup> proposed hydrogen–palladium (H<sub>2</sub>/Pd) and deuterium–palladium (D<sub>2</sub>/Pd) electrodes as new indicator electrodes for the potentiometric titrations acids and bases in ketones, nitriles, cyclic esters and alcohols. Similar behavior of the H<sub>2</sub>/Pd and D<sub>2</sub>/Pd indicator electrodes was observed in titrations acids and bases in some non-aqueous solvents (propylene carbonate,

ketones and nitriles).<sup>23–25</sup> Taking into account these facts, as well the simplicity of preparing an H<sub>2</sub>/Pd electrode (does not require deuterium oxide) and the good properties of tetrahydrofuran as a solvent for the titrations of acids, it was thought that an investigation of the possibility of applying a H<sub>2</sub>/Pd electrode as indicator electrode for determination of relative acidity scale of tetrahydrofuran and potentiometric titrations acids in this solvent could be useful.

### EXPERIMENTAL

#### Reagents

All employed chemicals were of analytical grade from Merck or Fluka. Tetrahydrofuran (THF, Fluka) with water content 0.03 % was used as the solvent without further purification. The acids used were benzoic acid, acetyl acetone,  $\alpha$ -naphthol, palmitic acid, maleic acid, phthalic acid and perchloric acid. Due to the instability of perchloric acid in THF, their solution was prepared in dioxane. Solutions of acids were used as primary standard (benzoic acid) or their concentrations were previously determined by titrating them against a standard solution of TBAH using visual (Thymol Blue indicator) or potentiometric end-point detection by means a glass-modified saturated calomel electrode (SCE) couple. Methanolic potassium hydroxide solutions were prepared according to Kreshkov.<sup>29</sup> TBAH (0.10 M) in a 2-propanol–methanol (10:1, v/v) was potentiometrically standardized against benzoic acid using a glass–SCE electrode pair. A Thymol Blue solution (0.1 %) in THF was used as an indicator.

#### Apparatus

The employed apparatus was described previously.<sup>27</sup> The potential changes during the titrations were followed with a Digital 870 pH meter, Dresden, Germany.

#### Electrodes

The hydrogen–palladium electrode was a spiral of 0.5 mm diameter palladium wire (99.9% pure; Johnson Matthey Metals, London) with surface area of 30 mm<sup>2</sup> saturated with hydrogen obtained by electrolysis of dilute sulfuric acid at a current 2 mA. The potential of the H<sub>2</sub>/Pd electrode prepared in this manner was measured as a function of time (Fig. 1).

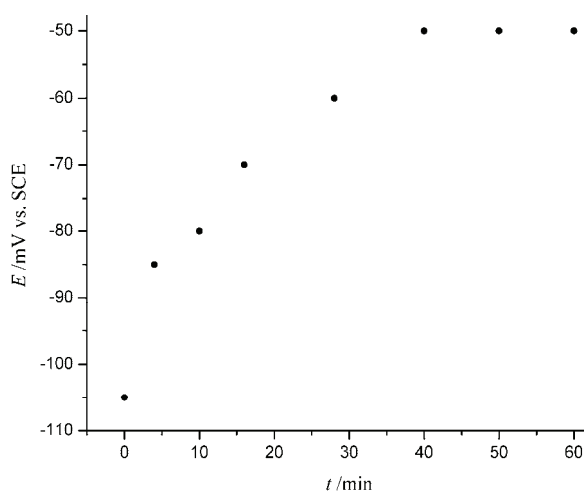


Fig. 1. Dependence of the H<sub>2</sub>/Pd electrode potential on time in THF medium.

As can be seen, if the H<sub>2</sub>/Pd electrode was used 40 min after saturation with hydrogen, a stable potential was established within a few minutes. The response time of the indicator H<sub>2</sub>/Pd electrode was determined by measuring the time that elapsed to reach a stable potential value after the H<sub>2</sub>/Pd electrode and the reference electrode were immersed in solutions from highly acidic (0.01 mol L<sup>-1</sup> perchloric acid) to highly basic (0.01 mol L<sup>-1</sup> TBAH). The H<sub>2</sub>/Pd electrode showed a relatively fast response time in the investigated solvent (less than 15 s). If the electrode was used frequently and for a long time, it was necessary to refill the H<sub>2</sub>/Pd electrode with hydrogen by electrolysis.

The glass electrode, type G-202C (Radiometer, Copenhagen, Denmark) was conditioned in THF before use. The electrode was stored in water when not in use and soaked for 30 min in THF before potentiometric measurements.

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

#### *Procedures*

*Determination of the relative acidity scale.* The relative acidity scale of THF was determined from the difference in the half-neutralization potentials of perchloric acid and TBAH.<sup>30</sup> Two electrode pairs, glass-SCE and H<sub>2</sub>/Pd-SCE, were used for the measurement of the half-neutralization potentials of the acid and base.

*Determination of the half-neutralization potential of perchloric acid.* THF (12.0 mL) was placed in the titration vessel and a measured volume of a standard solution of HClO<sub>4</sub> (1.00 mL) was added. The electrode pair, H<sub>2</sub>/Pd-SCE or glass-SCE, was immersed in the investigated solution and connected to a pH-meter. The solution of acid was then titrated to half neutralization with the standard solution of TBAH (0.1 M). The potential of half-neutralization of perchloric acid was read 15 min after thermostating (25±1 °C).

*The determination of the half-neutralization potential of TBAH.* THF (12.0 mL) was placed in the titration vessel and a measured volume of TBAH (1.00 mL) was added. The electrode system (H<sub>2</sub>/Pd-SCE or glass-SCE) was immersed in the solution and base was then titrated to half neutralization with a standard solution of perchloric acid (0.1 M). The half-neutralization potential of the base was also measured after thermostating of the solution.

*Potentiometric titrations.* THF (12.0 mL) was placed in the titration vessel and the required volume of the investigated acid and two drops of the indicator solution were added. The indicator electrode, either H<sub>2</sub>/Pd or glass electrode and a SCE as the reference one were immersed in the investigated solution and connected to a pH-meter. The solution was then titrated with standard solution of TBAH (potassium hydroxide or sodium methylate) and the potential was read after each addition of titrant. The test solution was stirred magnetically under a continuous stream of dry nitrogen.

## RESULTS AND DISCUSSION

The choice of the optimal conditions for potentiometric acid–base titrations in a non-aqueous medium can be made based on the relative acidity scale of the solvent. 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 is calculated from the difference between the half-neutralization potentials of a strong acid and a strong base in the given solvent. The  $E_s$  scale of a solvent defines the approximate potential ranges that could be used for potentiometric acid–base titrations under the determined expe-

perimental conditions (electrode pair, titrant, *etc.*). With increasing range of the  $E_s$  scale, the possibility of the titration of weak acids (bases) and differentiating titrations of mixtures acids (bases) in the solvent is increased.

The relative acidity scale of tetrahydrofuran (THF) was determined potentiometrically from the difference between the half-neutralization potentials of solutions of perchloric acid and TBAH of the same concentration.

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

The half-neutralization potentials of perchloric acid and TBAH were measured using a glass-SCE and  $\text{H}_2/\text{Pd}$ -SCE electrode pair. When a  $\text{H}_2/\text{Pd}$ -SCE electrode pair was used for measuring the half-neutralization potentials, a wider acidity scale of the solvent was obtained than when a glass-SCE electrode couple was applied (Table I).

TABLE I. Determination ( $n = 6$ ) of the relative acidity scale of THF. The potentials were measured using a glass-SCE and a  $\text{H}_2/\text{Pd}$ -SCE electrode pair at  $25.0 \pm 0.1$  °C

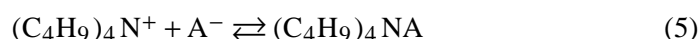
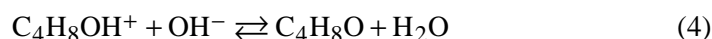
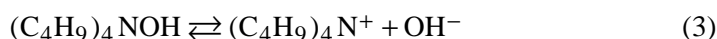
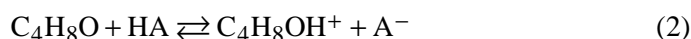
| Electrode pair                | $E_{1/2}(\text{HClO}_4) / \text{mV}$ | $E_{1/2}(\text{TBAH}) / \text{mV}$ | $E_s / \text{mV}$ |
|-------------------------------|--------------------------------------|------------------------------------|-------------------|
| Glass-SCE                     | $465 \pm 5$                          | $-415 \pm 0$                       | $880 \pm 5$       |
| $(\text{H}_2/\text{Pd})$ -SCE | $455 \pm 5$                          | $-700 \pm 5$                       | $1155 \pm 7$      |

Water lowered the range of the relative acidity scales. The addition of small amounts of water to the titrated solution had a large effect on the  $E_s$  scale of THF. Thus, after the addition of 1 % water, the relative acidity scale of THF was narrowed by 300 mV.

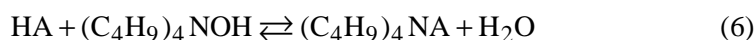
Based on the obtained experimental data for the relative acidity scale of the solvent, it is to be expected that the higher potential jumps at the end-point would be obtained if a  $\text{H}_2/\text{Pd}$  indicator electrode were used for the detection end-point in potentiometric titrations of acids in THF medium.

#### Potentiometric titrations of acids

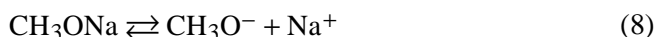
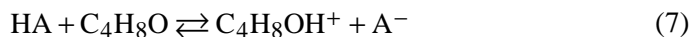
The behavior of the  $\text{H}_2/\text{Pd}$  electrode as an indicator electrode in THF was investigated by potentiometric titration of acids of different strengths and various structures with standard solutions of TBAH and sodium methylate. The titrations of acids with TBAH can be represented by the following equations:



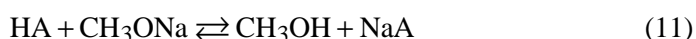
Summary:



and with sodium methylate by:



Summary:



As can be seen from the above equations, in the titration of an acid with TBAH, water, which has negative effect on the titration of weak acids in THF, is produced. In the titrations acids with a standard solution of sodium methylate, the presence of water in the titration solution is avoided.

The titration curves of the very weak acid  $\alpha$ -naphthol ( $pK_a$  in water is 9.30) in THF with sodium methylate and TBAH as titrants by applying the electrode couples  $\text{H}_2/\text{Pd}$ -SCE and glass-SCE are shown in Fig. 2. When a  $\text{H}_2/\text{Pd}$  electrode was used for the titration end-point (TEP) detection, the potential jumps with sodium methylate and TBAH as titrants amounted to 125 and 105 mV per 0.30 mL, respectively. In addition, it can be seen that the potential jumps were smaller when a glass electrode was applied (35 mV per 0.30 mL with sodium methylate and 75 mV per 0.30 mL with TBAH as titrants). The more significant decrease of the potential jump in the titration with sodium methylate as the titrant can be explained by the effect of the sodium ions on the glass electrode.

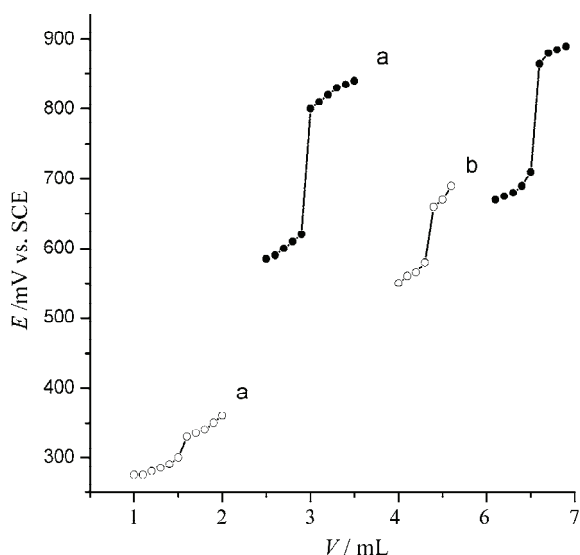


Fig. 2. The effect of the indicator electrode on the shape of the end-point in the potentiometric titration of  $\alpha$ -naphthol in THF. Electrode: empty circles – glass electrode; full circles –  $\text{H}_2/\text{Pd}$  electrode. Titrant: sodium methylate (a); TBAH (b).

The experimental results obtained in the titrations of the investigated acids are summarized in Table II. In all titrations, the potential jumps with a H<sub>2</sub>/Pd electrode were larger than those obtained with a glass electrode, which is in accordance with the experimentally determined range of the  $E_s$  scale of THF. The potentials during the titration and at the equivalence point were rapidly established (within a couple of minutes), and the change of the potential at the TEP coincided with that of the applied indicator color.

TABLE II. Potentiometric titration of acids in THF by application of the H<sub>2</sub>/Pd-SCE and glass-SCE electrode pairs

| Titrated acid      | Taken mg | Titration agent | Found ( $n = 5$ ), %   |             | Potential jump, mV per 0.30 mL |           |
|--------------------|----------|-----------------|------------------------|-------------|--------------------------------|-----------|
|                    |          |                 | H <sub>2</sub> /Pd-SCE | Glass-SCE   | H <sub>2</sub> /Pd-SCE         | Glass-SCE |
| Benzoic acid       | 12.21    | Na methylate    | 100.00±0.45            | 99.64±0.35  | 383                            | 25        |
|                    |          | TBAH            | 100.01±0.08            | 100.02±0.02 | 405                            | 390       |
| Acetyl acetone     | 7.84     | Na methylate    | 100.71±0.20            | 100.63±0.37 | 210                            | 86        |
|                    |          | TBAH            | 99.44±0.29             | 99.77±0.22  | 150                            | 130       |
| $\alpha$ -Naphthol | 12.03    | Na methylate    | 103.11±0.25            | 103.69±0.15 | 125                            | 35        |
|                    |          | TBAH            | 100.40±0.40            | 100.50±0.19 | 105                            | 75        |
| Palmitic acid      | 22.14    | Na methylate    | 99.77±0.10             | 99.93±0.64  | 305                            | 50        |
|                    |          | TBAH            | 97.78±0.04             | 97.21±0.26  | 120                            | 107       |

Water lowered the potential jumps at the equivalence point in the applied solvent. A more significant decrease of the potential jump was obtained when the content of water was increased by 1 %. The impact of water on the decrease of the potential jumps was much stronger in the titration of very weak acids.

The results obtained in the determination of the investigated acids (Table II) using a H<sub>2</sub>/Pd indicator electrode deviated on average by  $\pm 0.02$ – $0.50$  % in relation to those obtained with a glass electrode.

#### *Differential titrations of acids*

The differential titration of acids in mixture is possible if the difference between in the  $pK_a$  values of the acids in the employed solvent is sufficiently large. In cases where the  $pK_a$  values have not been reported, the choice can be made by comparing the titration curves of individual acids present in the mixture.

For differential titrations of acids in mixture in non-aqueous solvents, TBAH and alcoholic potassium hydroxide were recommended as suitable titrants.<sup>29</sup> Potassium hydroxide is advantageous over the other titration agents in the titrations of dicarboxylic acids. In a titration with alcoholic potassium hydroxide, the carboxylic groups of the dicarboxylic acid are neutralized separately due to the different solubility of the corresponding salts formed in the course of the titration. Therefore, the solvolysis of the potassium salts is considerably decreased and the sharpness of the end-point enhanced.



The potentiometric titrations of mixed acids in THF media were performed with methanolic potassium hydroxide as titrant using  $H_2/Pd$  indicator electrode. The potentiometric titration curves for the acid mixtures palmitic acid +  $\alpha$ -naphthol, maleic acid +  $\alpha$ -naphthol, maleic acid + phthalic acid and benzoic acid +  $\alpha$ -naphthol are shown in Fig. 3.

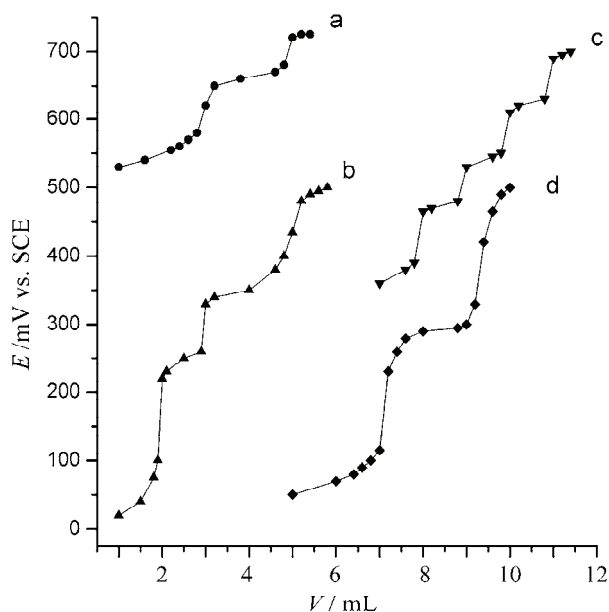


Fig. 3. Potentiometric titration curves acid mixtures in THF using an  $H_2/Pd$  electrode: a) palmitic acid +  $\alpha$ -naphthol; b) maleic acid +  $\alpha$ -naphthol; c) maleic acid + phthalic acid; d) benzoic acid +  $\alpha$ -naphthol. Titrant: KOH (a, b and c); TBAH (d).

The titration curve of the mixture palmitic acid +  $\alpha$ -naphthol has two potential jumps. The first jump corresponds to the neutralization of the palmitic acid and the second to the neutralization of  $\alpha$ -naphthol (Fig. 3, curve a). The titration curve of the mixture dicarboxylic maleic acid and  $\alpha$ -naphthol shows three potential jumps (Fig. 3, curve b); the first and second correspond to the neutralizations of the two carboxylic groups of maleic acid whereas the third corresponds to the neutralization of  $\alpha$ -naphthol. The potentiometric titration curve for a mixture of maleic acid and phthalic acid (Fig. 3, curve c) proves that the successive titration of a two dicarboxylic acids in a mixture is possible in this solvent.

The results of the potentiometric titrations of two component mixtures of acids under optimum experimental conditions are listed in Table III. The relative error of these determinations with respect to the individual determinations was less than 3 %.

#### CONCLUSIONS

Based on the presented results, it may be concluded that a  $H_2/Pd$  indicator electrode is very suitable for the potentiometric titrations of acids both indi-



vidually and as mixtures in tetrahydrofuran medium. In accordance with the range and position of the relative acidity scale of THF determined using an  $H_2/Pd$ -SCE electrode pair, the proposed electrode gives larger potential jumps at the titration end-point than a glass electrode. The advantages of the hydrogen-palladium electrode are rapid attainment of stable potential values, fast response, reproducibility and easy preparation.

TABLE III. The results of the potentiometric titration of acid mixtures in tetrahydrofuran using an  $H_2/Pd$  indicator electrode

| Acid mixture                       | Titrant | Taken mg | Found ( $n = 5$ ) % | Potential jump, mV per 0.30 mL |
|------------------------------------|---------|----------|---------------------|--------------------------------|
| Benzoic acid + $\alpha$ -naphthol  | ТВАН    | 12.8     | 100.33±0.10         | 155                            |
|                                    |         | 13.41    | 99.43±0.32          | 80                             |
| Palmitic acid + $\alpha$ -naphthol | КОН     | 26.67    | 98.65±0.13          | 75                             |
|                                    |         | 13.84    | 100.62±0.02         | 30                             |
| Maleic acid + $\alpha$ -naphthol   | КОН     | 11.03    | 100.00±0.03         | 125                            |
|                                    |         | 13.84    | 103.11±0.03         | 40                             |
| Maleic acid + phthalic acid        | КОН     | 11.03    | 100.00±0.10         | 60                             |
|                                    |         | 15.70    | 102.48±1.20         | 70                             |

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#### ИЗВОД

#### ПРИМЕНА ВОДОНИК/ПАЛАДИЈУМОВЕ ЕЛЕКТРОДЕ ЗА ПОТЕНЦИОМЕТРИЈСКА КИСЕЛИНСКО-БАЗНА ОДРЕЂИВАЊА У ТЕТРАХИДРОФУРАНУ

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Испитана је примена водоник-паладијумове индикаторске електроде ( $H_2/Pd$ ) за одређивање релативне скале киселости тетраhydroфурана (THF) и потенциометријске титрације киселина у овом растварачу. Релативна киселинска скала ( $E_s$ , mV) је одређена из полунутрализационих потенцијала перхлорне киселине и тетрабутиламонијум-хидроксида (ТВАН) применом електродних парова  $H_2/Pd$ -ЗКЕ и стаклена електрода-ЗКЕ. Експериментално добијена вредност  $E_s$  скале THF употребом  $H_2/Pd$ -ЗКЕ електродног пара износи 1155 mV, а употребом електродног пара стаклена електрода-ЗКЕ 880 mV.  $H_2/Pd$  индикаторска електрода је употребљена за потенциометријске титрације киселина (бензоева киселина, палмитинска киселина, малеинска киселина, ацетил-ацетон и  $\alpha$ -нафтол) и смеше киселина (бензоева киселина +  $\alpha$ -нафтол, палмитинска киселина +  $\alpha$ -нафтол, малеинска киселина +  $\alpha$ -нафтол и малеинска + фтална киселина) стандардним раствором ТВАН. Поред ТВАН, натријум-метилат и калијум-хидроксид су се показали веома погодним титрантима за титрацију појединачних киселина и смеше киселина. Релативна грешка одређивања киселина у смеси је мања од 3 %. Резултати одре-

ђивања су у сагласности са оним добијеним применом конвенционалне стаклене електроде. Предности водоник–паладијумове електроде у потенциометријским киселинско–базним одређивањима у односу на стаклену электроду су у следећем: ова електрода даје већи опсег релативне скале киселости THF, веће скокове потенцијала на завршној тачки титрације и брз одговор. Поред тога, електрода има мали отпор, једноставно се припрема и може бити коришћена за титрацију раствора малих запремина.

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