Journal of the Serbian Chemical Society

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J. Serb. Chem. Soc. *78* (8) 1203–1212 (2013)
JSCS–4491

UDC 54–32+53.085.4:544.6.076.32–
546.11’98:543.554
Original scientific paper

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

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(Received 27 September 2012, revised 9 February 2013)

Abstract: The application of the hydrogen–palladium electrode (H_2/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_2/Pd–SCE and glass–SCE electrode pairs. The experimentally obtained value of the E_s scale of THF with the H_2/Pd–SCE electrode pair was 1155 mV, while that obtained with the glass–SCE electrode pair was 880 mV. By using an H_2/Pd indicator electrode, the individual acids (benzoic acid, palmitic acid, maleic acid, acetyl acetone and α-naphthol) and two component acid mixtures (benzoic acid + α-naphthol, palmitic acid + α-naphthol, maleic acid + α-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_2/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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doi: 10.2298/JSC120927018J

INTRODUCTION

Tetrahydrofuran (THF) is a dipolar aprotic protophilic solvent with a low relative permittivity (ε_r = 7.39 at 298.15 K), a dipole moment of 5.4×10^{-30} C m and a large acidity scale (34.7 pK_S). 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).[1] THF is an excellent solvent for dissolving a wide variety of substances, such as ionic species, organometallic compounds and many polymeric materials.[2–4] The solvatochromic properties of THF (hydrogen-bond donor capacity, α = 0, polarity, π = 0.58, and low hydrogen-bond acceptor capacity, β = 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.[5–9]

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 alcohols, acetophenones, esters, anilides, carbamates and lactams, can be titrated as very weak acids.[10] 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[4] determined coulometrically the weak acrylic acid content incorporated in a copolymer with electrically generated tetrabutylammonium hydroxide (TBAH) in THF. Meng-Liang and Chang-Yi[11] reported the potentiometric micro-titration of *p*-phthalic acid and Barron and Barbosa[6] performed differential potentiometric titrations of acids in THF medium.

A glass electrode in 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 same 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.[12–21]

Mihajlović *et al.*[22–28] proposed hydrogen–palladium (H_2/Pd) and deuterium–palladium (D_2/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_2/Pd and D_2/Pd indicator electrodes was observed in titrations acids and bases in some non-aqueous solvents (propylene carbonate, ketones and nitriles).[23–25] Taking into account these facts, as well the simplicity of preparing an H_2/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_2/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, α-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.[29] 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.[27] 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^2 saturated with hydrogen obtained by electrolysis of dilute sulfuric acid at a current 2 mA. The potential of the H_2/Pd electrode prepared in this manner was measured as a function of time (Fig. 1).

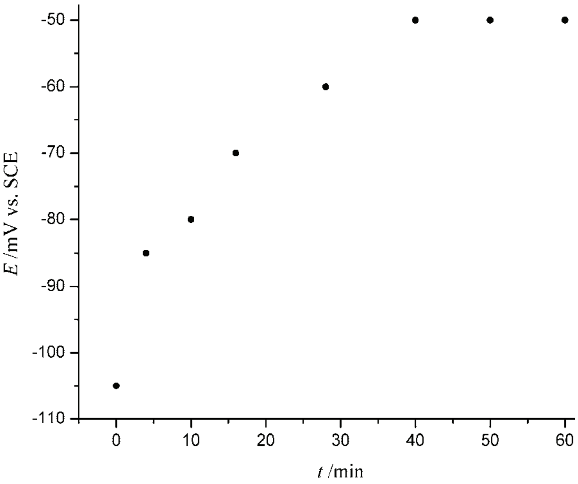

Fig. 1. Dependence of the H_2/Pd electrode potential on time in THF medium.

As can be seen, if the H_2/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_2/Pd electrode was determined by measuring the time that elapsed to reach a stable potential value after the H_2/Pd electrode and the reference electrode were immersed in solutions from highly acidic (0.01 mol L^{-1} perchloric acid) to highly basic (0.01 mol L^{-1} TBAH). The H_2/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_2/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.[30] Two electrode pairs, glass–SCE and H_2/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 $HClO_4$ (1.00 mL) was added. The electrode pair, H_2/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_2/Pd–SCE or glass–SCE) was immersed in the solution and base was than 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_2/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 experimental 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.

$$E_s = E_{1/2}(\mathrm{HClO_4}) - E_{1/2}(\mathrm{TBAH}) \tag{1}$$

The half-neutralization potentials of perchloric acid and TBAH were measured using a glass–SCE and H_2/Pd–SCE electrode pair. When a H_2/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 H_2/Pd–SCE electrode pair at 25.0±0.1 °C

Electrode pair	$E_{1/2(\mathrm{HClO_4})}$ / mV	$E_{1/2(\mathrm{TBAH})}$ / mV	E_s / mV
Glass–SCE	465±5	–415±0	880±5
(H_2/Pd)–SCE	455±5	–700±5	1155±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 H_2/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 H_2/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:

$$\mathrm{C_4H_8O + HA \rightleftarrows C_4H_8OH^+ + A^-} \tag{2}$$

$$\mathrm{(C_4H_9)_4NOH \rightleftarrows (C_4H_9)_4N^+ + OH^-} \tag{3}$$

$$\mathrm{C_4H_8OH^+ + OH^- \rightleftarrows C_4H_8O + H_2O} \tag{4}$$

$$\mathrm{(C_4H_9)_4N^+ + A^- \rightleftarrows (C_4H_9)_4NA} \tag{5}$$

Summary:

$$\mathrm{HA + (C_4H_9)_4NOH \rightleftarrows (C_4H_9)_4NA + H_2O} \tag{6}$$

and with sodium methylate by:

$$HA + C_4H_8O \rightleftarrows C_4H_8OH^+ + A^- \tag{7}$$

$$CH_3ONa \rightleftarrows CH_3O^- + Na^+ \tag{8}$$

$$C_4H_8OH^+ + CH_3O^- \rightleftarrows C_4H_8O + CH_3OH \tag{9}$$

$$Na^+ + A^- \rightleftarrows NaA \tag{10}$$

Summary:

$$HA + CH_3ONa \rightleftarrows CH_3OH + NaA \tag{11}$$

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 α-naphthol (pK_a in water is 9.30) in THF with sodium methylate and TBAH as titrants by applying the electrode couples H_2/Pd–SCE and glass–SCE are shown in Fig. 2. When a H_2/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.

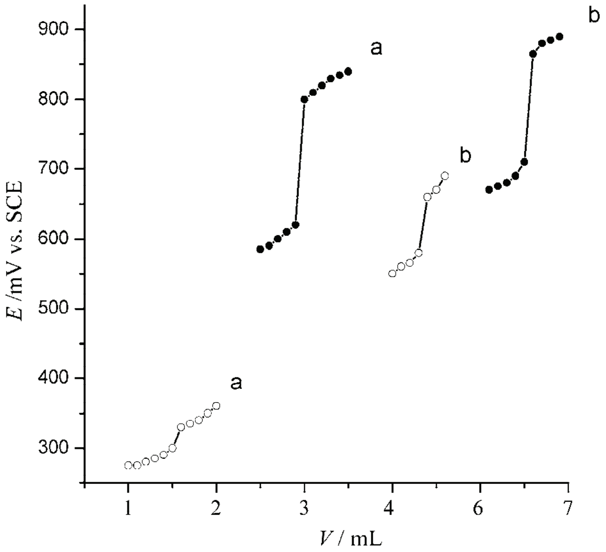

Fig. 2. The effect of the indicator electrode on the shape of the end-point in the potentiometric titration of α-naphthol in THF. Electrode: empty circles – glass electrode; full circles – H_2/Pd electrode. Titrant: sodium methylate (a); TBAH (b).

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_2/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_2/Pd–SCE and glass–SCE electrode pairs

Titrated acid	Taken mg	Titration agent	Found (n = 5), %		Potential jump, mV per 0.30 mL	
			H_2/Pd–SCE	Glass–SCE	H_2Pd–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
α-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_2/Pd indicator electrode deviated on average by ±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.[29] 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 titrations curves for the acid mixtures palmitic acid + α-naphthol, maleic acid + α-naphthol, maleic acid + phthalic acid and benzoic acid + + α-naphthol are shown in Fig. 3.

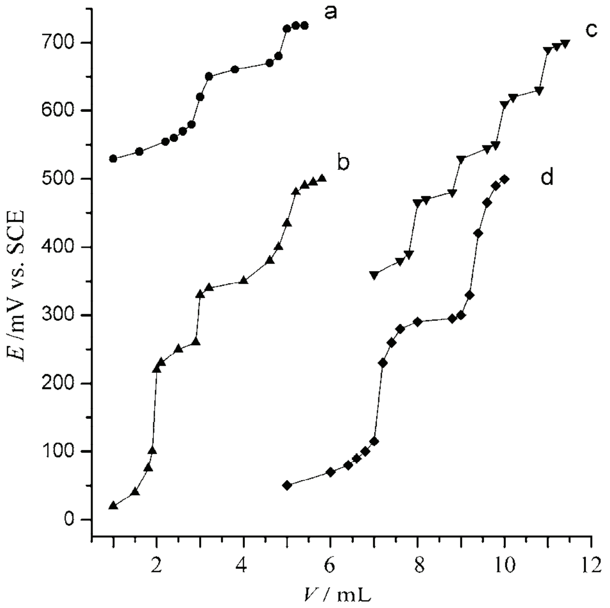

Fig. 3. Potentiometric titration curves acid mixtures in THF using an H_2/Pd electrode: a) palmitic acid + α-naphthol; b) maleic acid + α-naphthol; c) maleic acid + phthalic acid; d) benzoic acid + α-naphthol. Titrant: KOH (a, b and c); TBAH (d).

The titration curve of the mixture palmitic acid + α-naphthol has two potential jumps. The first jump corresponds to the neutralization of the palmitic acid and the second to the neutralization of α-naphthol (Fig. 3, curve a). The titration curve of the mixture dicarboxylic maleic acid and α-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 α-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 individually 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 + α-naphthol	TBAH	12.8	100.33±0.10	155
		13.41	99.43±0.32	80
Palmitic acid + α-naphthol	KOH	26.67	98.65±0.13	75
		13.84	100.62±0.02	30
Maleic acid + α-naphthol	KOH	11.03	100.00±0.03	125
		13.84	103.11±0.03	40
Maleic acid + phthalic acid	KOH	11.03	100.00±0.10	60
		15.70	102.48±1.20	70

Acknowledgement. The authors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Project No. 172051).

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 тетрахидрофурана (THF) и потенциометријске титрације киселина у овом растварачу. Релативна киселинска скала (E_s, mV) је одређена из полунеутрализационих потенцијала перхлорне киселине и тетрабутиламонијум-хидроксида (TBAH) 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 α-нафтол) и смеше киселина (бензоева киселина + α-нафтол, палмитинска киселина + α-нафтол, малеинска киселина + α-нафтол и малеинска + фтална киселина) стандардним раствором TBAH. Поред TBAH, натријум-метилат и калијум-хидроксид су се показали веома погодним титрантима за титрацију појединачних киселина и смеше киселина. Релативна грешка одређивања киселина у смеши 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 електроду 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.

(Примљено 27. септембра 2012, ревидирано 9. фебруара 2013)

REFERENCES

1. I. M. Kolthoff, *Anal. Chem.* **46** (1974) 1992
2. S. Mah, D. You, H. Cho, S. Choi, J.-H. Shin, *J. Appl. Polym. Sci.* **69** (1998) 611
3. S. Hanesian, N. Moitessier, S. Wilmouth, *Tetrahedron* **56** (2000) 7643
4. C. E. Champion, D. G. Bush, *Anal. Chem.* **45** (1973) 640
5. J. Barbosa, D. Barron, E. Bosch, M. Roses, *Anal. Chim. Acta* **265** (1992) 157
6. D. Barron, J. Barbosa, *Anal. Chim. Acta* **403** (2000) 339
7. J. Barbosa, D. Barron, E. Bosch, M. Roses, *Anal. Chim. Acta* **264** (1992) 229
8. G. Garrido, E. Koort, C. Rafols, E. Bosch, T. Radima, I. Leito, M. Roses, *J. Org. Chem.* **71** (2006) 9062
9. G. Garrido, M. Roses, C. Rafols, E. Bosch, *J. Solution Chem.* **37** (2008) 689
10. D. D. Clyde, *Anal. Chem.* **52** (1980) 1308
11. W. Meng-Liang, W. Chang-Yi, *Anal. Chim. Acta* **198** (1987) 325
12. C. J. Lintner, R. F. Schleif, T. Higuchi, *Anal. Chem.* **22** (1950) 534
13. E. J. Greenhow, B. F. Al Mudarris, *Talanta* **22** (1975) 417
14. K. Izutsu, T. Nakamura, T. Arai, M. Ohmaki, *Electroanalysis* **7** (1995) 884
15. K. Izutsu, M. Ohmaki, *Talanta* **43** (1996) 643
16. K. Izutsu, H. Yamamoto, *Anal. Sci.* **12** (1996) 905
17. M. Antonijević, B. Vukanović, R. Mihajlović, *Talanta* **39** (1992) 809
18. Lj. V. Mihajlović, R. P. Mihajlović, M. M. Antonijević, B. V. Vukanović, *Talanta* **64** (2004) 879
19. Lj. Mihajlović, S. Nikolić-Mandić, B. Vukanović, R. Mihajlović, *Anal. Sci.* **25** (2009) 437
20. Lj. Mihajlović, S. Nikolić-Mandić, B. Vukanović, R. Mihajlović, *J. Solid State Electrochem.* **13** (2009) 895
21. R. P. Mihajlović, Z. D. Stanić, *J. Solid State Electrochem.* **9** (2005) 558
22. V. J. Vajgand, R. P. Mihajlović, R. M. Džudović, Lj. N. Jakšić, *Anal. Chim. Acta* **202** (1987) 231
23. R. Mihajlović, V. Vajgand, R. Džudović, *Talanta* **38** (1991) 673
24. R. P. Mihajlović, Lj. N. Jakšić, R. M. Džudović, *J. Serb. Chem. Soc.* **61** (1996) 689
25. R. Mihajlović, Z. Simić, Lj. Mihajlović, A. Jokić, M. Vukašinović, N. Rakićević, *Anal. Chim. Acta* **318** (1996) 287
26. R. Mihajlović, Z. Stanić, M. Antonijević, *Anal. Chim. Acta* **497** (2003) 143
27. Lj. V. Mihajlović, S. D. Nikolić-Mandić, R. P. Mihajlović, *J. Appl. Electrochem.* **39** (2009) 1917
28. Lj. V. Mihajlović, S. D. Nikolić-Mandić, I. Đ. Pantić, R. P. Mihajlović, *J. Solid State Electrochem.* **14** (2010) 123
29. A. P. Kreshkov, L. N. Bykova, N. A. Kazaryan, *Kislotno-osnovnoe titrovanie v nevodnikh rastvorakh*, Khimiya, Moscow, 1967, p. 37
30. A. P. Kreshkov, *Analiticheskaya khimiya nevodnykh rastvorov*, Khimiya, Moscow, 1982, p. 183.