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ORIGINAL PAPER

A deuterium–palladium electrode as a new sensor in non-aqueous media: the potentiometric titration of weak acids in alcohols

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Abstract A deuterium–palladium electrode was employed as a new indicator electrode for the titration of weak acids in *tert*-butanol and iso-propanol. The investigated electrode showed a linear dynamic response for *p*-toluenesulfonic acid in the concentration range from 0.1 to 0.001 mol L^{-1}, with a Nernstian slope of 53.0 mV per decade in *tert*-butanol. The potential in the course of the titration and at the titration end-point (TEP) was rapidly established. Potassium hydroxide and tetrabutylammonium hydroxide (TBAH) proved to be very suitable titrating agents for these titrations. The response time was less than 10–11 s and the lifetime of the electrode was limitless. The experimental results obtained for the proposed electrochemical sensor and a conventional glass electrode were in good agreement. The advantages of the electrode are long-term stability, fast response, reproducibility, and easy preparation.

Keywords Deuterium–palladium electrode · Potentiometry · Sensors · Non-aqueous media · Alcohols

1 Introduction

In recent years, non-aqueous solvents have been widely used in analytical chemistry with the rapid development of non-aqueous analytical techniques and methods. Among non-aqueous solvents, *tert*-butanol and iso-propanol have often been used as the medium in numerous investigations.

tert-Butanol is a very useful solvent for the titration of weak acids with tetrabutylammonium hydroxide (TBAH) [1–4] and for differentiating titration involving carboxylic acids and phenol. Due to its excellent solvent characteristics, fundamental information on acid–base equilibria would be very useful [5–10]. In this solvent, Fritz and Gainer [11] coulometrically titrated mineral acids, sulfonic acids, carboxylic acid, enols, imides, and phenols with electrically generated TBAH.

Iso-propanol, like *tert*-butanol, is a very useful solvent for the titration of weak acids [4, 12], for the determination of many organic compounds [2, 7, 13–16], for the determination of pK_a value of azolactone dyes [6] and hydroxylated benzoic acids and cinnamic acids [16]. Aktaş et al. [17] conductimetrically and potentiometrically titrated hydroxycinnamic acids using triethylamine and TBAH. Hine et al. [18] determined the relative acidity of five indicators in iso-propanol solution. Yalçin et al. [19] determined the pK_a values of 6-semicarbazone 9–17 monomethyl-substituted octadecanoic acids using the potentiometric titration method. Gündüz et al. [20] potentiometrically titrated symmetrical aliphatic dicarboxylic acids and some of their binary mixtures. Bosch et al. [10] determined the dissociation constants of some anti-inflammatory agents in this solvent. Canel et al. [21] conductimetrically and potentiometrically investigated the effect of solvents and titrant on the formation of homoconjugates and arrived at the conclusion that homoconjugation was low in this solvent. André and Romero [22] determined the acidic groups of fulvic acid from lignite by potentiometric titration in this solvent. Johansson [23] titrated very weak acids in this solvent using a

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coulometrically generated base, while Cooksey et al. [24] generated the base by reduction of solvent, oxygen, and traces of water.

As it can be seen from the literature data, *tert*-butanol and iso-propanol are extensively used as a medium in the potentiometric determinations of many acidic substances. A glass electrode is most frequently used as the indicator electrode, both in aqueous and non-aqueous media. In an aqueous environment, glass electrodes are very popular due to their high selectivity and dynamic pH range. However, in spite of the distinctive potential characteristic of pH-glass electrodes and their use in routine pH measurements for many years, they have certain limitation, such as high resistance, fragility, instability in hydrofluoric acid solution or acidic solution of fluorides, and contamination of the membrane. In non-aqueous media, these electrodes show certain undesirable features, e.g., the potential response of a glass electrode in non-aqueous solution is often very slow. In addition, the electrodes have a limited useful life when employed in non-aqueous titrations because the solvents dehydrate the glass membrane, thereby reducing its affinity for, or response to, hydrogen ions.

These disadvantages of glass electrodes have led to intensive research for alternative pH electrodes in water and in non-aqueous solution. For this purpose, Lintner et al. [25] used a platinum electrode for titration in tetrahydrofuran with lithium aluminum hydride. A platinum electrode was also used by Katz and Glenn [26] for titrations in ethylenediamine. Harlow et al. [27] used an anodically polarized platinum wire and antimony as an indicator electrode for the titration of very weak acids in some solvent. Greenhow and Al-Mudarris [28] used metal and metalloid indicator electrodes (aluminium, gallium, indium, thallium, carbon, silicon, germaniumn, tin, lead, arsenic, antimony, and bismuth) for the potentiometric titration of solution of benzoic acid and 3,5-xylenol in dimethylformamide and 4-methyl-2-pentanone, and Izutsu et al. [29–31] used silicone nitride (Si_3N_4), tantalum oxide (Ta_2O_5), and iridium oxide pH sensors in non-aqueous solution. However, redox interference is a known problem with metal oxide electrodes.

In previous studies, many deficiencies of the glass electrode (high resistance, fragility, contamination of the membrane, alkaline error, and dehydration of the glass membrane in non-aqueous media) were eliminated using natural monocrystalline pyrite, chalcopyrite, and galena as electrochemical sensors for the potentiometric titrations of weak acids in pyrrolidone, N,N-dimethylformamide, pyridine, γ-butyrolactone, and propylene carbonate [32, 33].

However, the proposed electrode cannot be applied in potentiometric titration in the solvents that dissolve crystal carrier. In these solvents, sensor carrier must be made of Teflon or some other material which is not soluble in the investigated solvent.

Investigation by Fleishman and Pons [34] on the fusion of deuterium in palladium inspired us to examine the possibility of the analytical application of the deuterium–palladium (D_2/Pd) electrode as a generator electrode in the coulometric–potentiometric determination of bases in propylene carbonate and ketone media [35, 36].

In this study, the possibility of applying D_2/Pd as a sensor (sensor carrier is palladium, the metal that is chemically inert in organic solvents) for the potentiometric determination of weak organic acids in *tert*-butanol and iso-propanol as solvents was investigated.

2 Experimental

2.1 Reagents

All the chemicals used in the present study were of analytical reagent from Merck, Fluka, or Baker.

Deuterium oxide (99.8% pure, ZGN Chemical Radioisotope Division), *tert*-butanol and iso-propanol (Fluka) were *puriss* p.a. purity: *tert*-butanol ($\geq$99.7), with a water content $\leq$0.01% and iso-propanol ($\geq$99.8%) with water content $\leq$0.1%. These solvent were used without further purification. The water content in the applied solvents was measured by Karl Fischer titration.

Solutions of the acids (α-nitroso-β-naphthol, benzoic acid, stearic acid) were prepared by weighing a definite amount of an acid and dissolving it in the titration solvent. The concentration of the acid solutions was controlled by titration with standard 0.1 mol L^{-1} Bu_4NOH (TBAH) using visual end-point detection or potentiometric end-point detection by means of a glass electrode-modified SCE couple.

p-Toluenesulfonic acid monohydrate was dried under vacuum over P_2O_5 at 70–80 °C for several days.

Tetrabutylammonium hydroxide (laboratory-reagent grade) 0.1 mol L^{-1} in iso-propanol–methanol (10:1 v/v) (Fluka) was standardized against benzoic acid with Thymol Blue as the indicator.

The Thymol Blue indicator solution was prepared by dissolving 0.1 g Thymol Blue in 100 mL of methanol.

Potassium hydroxide (laboratory-reagent grade) 0.1 mol L^{-1} in ethanol (Riedel-de Haën) was standardized against benzoic acid with Thymol Blue as indicator.

The required volume of the acid was measured by means of a micro burette with a PTEF stopcock; 2–3.00 mL of the investigated acids was measured.

All measurements were carried out at room temperatures between 20 and 25 °C, for *tert*-butanol 28 °C.

2.2 Electrodes

The indicator D_2/Pd electrode was made of conventional palladium wire (1 cm) sealed into a glass tube by means of platinum and connected with a pH meter, using a contact made of copper wire. The platinum used for the connection with the Pd wire was never exposed to the solution, hence it had no effect upon the potentials measured. The wire was saturated with gaseous deuterium, obtained by electrolyzing deuterium oxide.

The response of the indicator D_2/Pd electrode in the alcohols was compared with that of a conventional glass electrode type G-202C (Radiometer, Copenhagen). The glass electrode was conditioned in the appropriate solvent before used.

The reference electrode was a modified SCE. The modification of the SCE electrode of the type 401 (Radiometer, Copenhagen) realized by the replacement of its inner solution with methanolic potassium chloride solution. The solution was vigorously stirred with a magnetic stirrer during the titration.

2.3 Apparatus

The apparatus used to follow the potential changes of the D_2/Pd electrode with time and for end-point detection with either a D_2/Pd electrode-SCE or a glass electrode-SCE couple is shown in Fig. 1. The potential changes during the titration were followed with a Digital 870 pH-meter, Dresden.

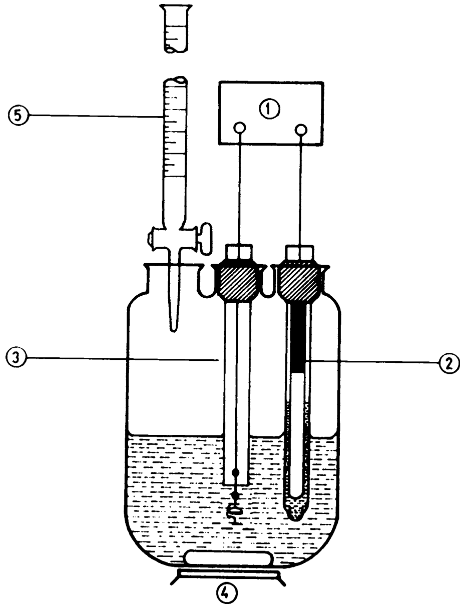

Fig. 1 Scheme of the apparatus for potentiometric titration of acid: (1) pH meter; (2) reference electrode; (3) indicator electrode (D_2/Pd); (4) magnetic stirrer; (5) burette

The same apparatus with an additional temperature-controlled cell was used to follow the potential changes of the employed electrode as a function of the concentration of *p*-toluenesulfonic acid.

2.4 Procedure

2.4.1 Potential measurement

The stationary potential measurements of the D_2/Pd electrode were performed in a series of *p*-toluenesulfonic acid in the concentration range of 0.1–0.001 mol L^{-1}. The potential of D_2/Pd electrode with time was followed in a temperature-controlled cell (25 ± 0.1 and 28 ± 0.1 °C). The ionic strength of the solution was maintained with 0.05 mol L^{-1} tetrabutylammonium perchlorate. The potential values determined in this way were used to calculate the slopes.

The change of the potential of the D_2/Pd electrode with time was followed in the required solvent. This indicator electrode was coupled with a modified SCE as the reference electrode.

2.4.2 Potentiometric titration

A certain volume (10 mL) of the required solvent which had previously been titrated was placed in the titration vessel and a measured volume of the investigated acid, and two drops of the indicator solution were added. The indicator electrode, either D_2/Pd or glass electrode and a modified calomel electrode as the reference were immersed in the solution and connected to a pH meter. The solution was then titrated potentiometrically by adding 0.05 or 0.1 mL increments of 0.1 mol L^{-1} TBAH (potassium hydroxide) and the potential was read after each addition of the titrant. The potential measurements were made in 2-min intervals during the course of the titration. The titration end-points were determined by the classical method from the second derivative.

3 Results and discussion

3.1 Mechanism

The D_2/Pd electrode, as well as the H_2/Pd electrode, is very similar to a hydrogen electrode (with platinum). However, palladium has one significant feature, i.e., the capability to absorb (dissolve into itself) molecular hydrogen and deuterium.

The potential of this electrode (as in the case of Pd/H_2) is given by the expression:

$$E_D = E^o_D + 0.05916 \log a_{H^+}, \quad (1)$$

where $E^o_D 4.31$ mV [37]

From expression (1), it can be seen that the potential of a D_2/Pd electrode depends (in water) on the activity of H_3O^+ ions. Equation 1 can also be applied in alcohols containing weak organic acids.

3.2 Characteristics of a D_2/Pd ISE electrode

If an ISE electrode is to be applied as a sensor for quantitative measurements in a non-aqueous environment, the following conditions should be fulfilled: a stable potential in acid and base medium, an adequate slope, sensitive, short response time and a long-stability (lifetime), and repeatability.

3.3 Potential of the D_2/Pd electrode

In all the investigated solutions, a stable potential of the D_2/Pd electrode was attained in less than 4–5 min (Fig. 2).

3.4 Slope of the potential response of a D_2/Pd electrode

The potential of the D_2/Pd electrode was read using a series of concentrations of *p*-toluenesulfonic acid in the range 0.1–0.001 mol L^{-1} in a temperature-controlled cell (25 ± 0.1 °C for iso-propanol and 28 ± 0.1 °C for *tert*-butanol). The ionic strength of the solutions was maintained at 0.05 mol L^{-1} with tetrabutylammonium perchlorate. The values of the slope of the potential in *tert*-butanol were 53.0 mV per decade (similar slopes were obtained for iso-propanol) for the given range of concentrations (Fig. 3). Since the D_2/Pd electrode exhibits sub-Nernstian dependences, it cannot be used for the measurement of the pH of a solution, but since the potential of the D_2/Pd electrode as an indicator electrode is very stable with respect to time, it can be successfully applied for the titration of acids in *tert*-butanol and iso-propanol as solvents.

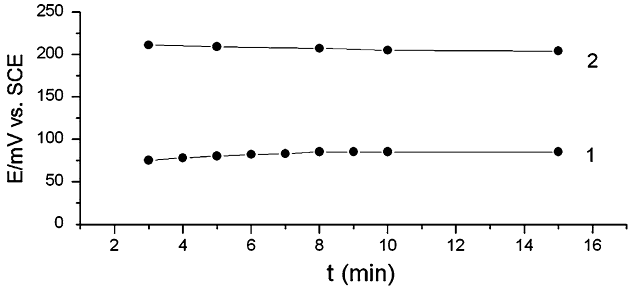

Fig. 2 Plots of the D_2/Pd electrode potential versus time (*p*-toluenesulfonic acid) in: (1) iso-propanol; (2) *tert*-butanol

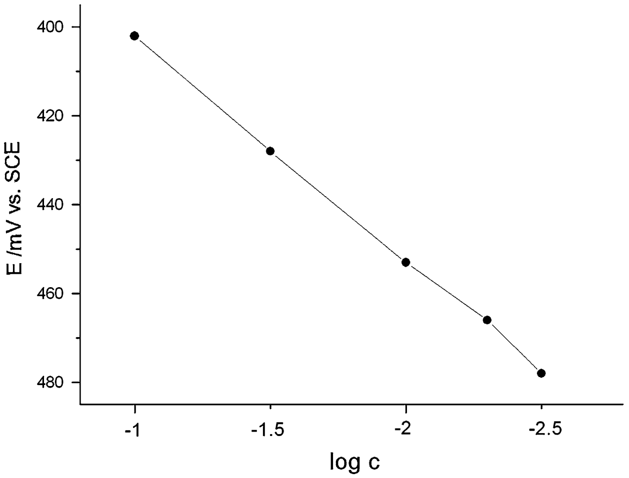

Fig. 3 Plots of the D_2/Pd electrode potential versus log c (mol L^{-1} *p*-toluenesulfonic acid) in *tert*-butanol

3.5 Response time of the electrodes

The response time of the D_2/Pd electrode was determined by recording the time that elapsed before a stable potential value was attained, after the D_2/Pd electrode and the reference electrode (modified SCE) were immersed in calibration solutions from highly acidic (0.05 mol L^{-1} of *p*-toluenesulfonic acid) to highly basic (0.05 mol L^{-1} TBAH) solutions. The change of the electrode potential from the acidic (*p*-toluenesulfonic acid) to the basic region (TBAH) ranged from +373 to −376 mV (2-propanol). The response time was 10 s for iso-propanol and 11 s for *tert*-butanol. These results were within the limits of the results obtained by many hydrogen electrodes giving a linear response within the same pH range. In conclusion, the response time of the prepared D_2/Pd electrode was compatible with most similar electrodes reported in the literature [38, 39].

3.6 Long-term stability (lifetime) and repeatability

The lifetime of the electrode was determined by raising the potential values of the calibration solution (*p*-toluenesulfonic acid) and plotting the calibration curves for a period of several years. The slope of the electrode remained constant. However, if the electrode was used frequently and for a long time, it was necessary to refill the D_2/Pd electrode with deuterium by electrolysis. Then after washing and drying the D_2/Pd electrode was suitable for further use.

In order to establish the efficiency of use of the D_2/Pd electrode in potentiometric titrations and the repeatability of the results obtained, the titration of benzoic acid with potassium hydroxide was selected as a model and it was repetitively carried out for six times and the end point was

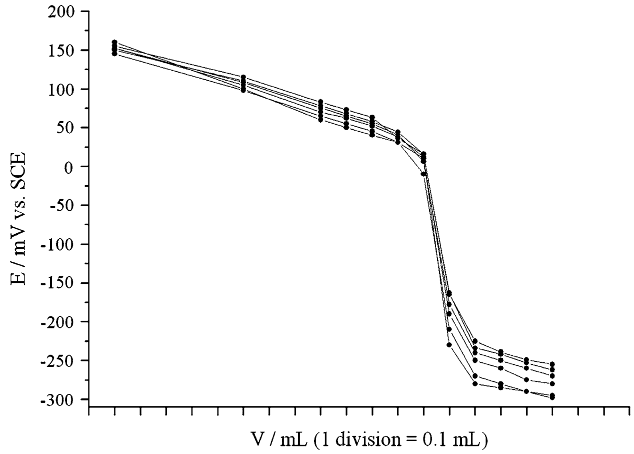

Fig. 4 Six titration curves for 2 mL benzoic acid solution ($\sim$0.09 mol L^{-1}), by standard potassium hydroxide solution of 0.1 mol L^{-1}, using D_2/Pd as an indicator electrode in iso-propanol

monitored by using this electrode. The results obtained for the titration of benzoic acid with potassium hydroxide were shown in Fig. 4. The relative standard deviation (RSD) for the end point determination of titration was found to be 0.25%. The values of RSD for the end point determination of titrations of different acids are shown in the Table 2.

3.7 Analytical application

3.7.1 *Titration of acids in tert-butanol and iso-propanol*

Tetrabutylammonium hydroxide and potassium hydroxide are most often used as the titrant for the titration of acidic substances in *tert*-butanol and iso-propanol as solvents with a glass electrode as the indicator. Since the D_2/Pd electrode is proposed as a new sensor instead of a glass electrode in the determination of the TEP, KOH in anhydrous methanol and TBAH in a mixture of iso-propanol–methanol were used as the titrant in all the present investigations of the behavior of the D_2/Pd electrode as the indicator in *tert*-butanol and iso-propanol as solvents.

The practical utility of the proposed sensor was tested by its use as an indicator electrode for the titration of weak acids of different strengths, i.e., benzoic, stearic acids, and α-nitroso-β-naphthol, with methanolic potassium hydroxide and TBAH.

The neutralization reaction of acids in non-aqueous solvent with TBAH and KOH was presented in our previous papers [32, 33]. As can be seen in those reaction equations, the produced water has a negative effect on the titration of the examined acids with KOH and TBAH. In dilute aqueous solution, the activity of the water would be constant, but if the Nernst equation is applied in non-aqueous solution (in alcohols), the developed potential would be related to the activities of both the hydrogen ions and the water:

$$E = E^{o} + \frac{RT}{nF} \ln \frac{a^{k}_{H_3O^+}}{(a_{H_3O})^{2k}}. \qquad (2)$$

When solution of KOH and TBAH is used as the titrants in non-aqueous systems (alcohols), water is produced during the neutralization of the acids and the potential changes are not simply related to the activity of the hydrogen ions only. However, since the concentration of the water increases during the titration and that of the acid decreases, the potential change should be greater than the corresponding one when the water concentration remains constant. The theoretical value for this increase in the potential change can be calculated by inserting the appropriate date into the Nernst equation.

The titration curves of benzoic and stearic acids and α-nitroso-β-naphthol in *tert*-butanol and iso-propanol as the solvents with potassium hydroxide and TBAH as titrants with the application of the electrode couples D_2/Pd-SCE and glass-SCE are shown in Figs. 5 and 6. While titrating stearic acid with TBAH, for example, the potential jump at the TEP amounted 324 mV/0.3 mL in iso-propanol (265 mV/0.3 mL with a glass electrode) and 303 mV/0.3 mL in *tert*-butanol (291 mV/0.3 mL with a glass electrode) when a D_2/Pd electrode is used as the sensor (Table 1). When stearic acid was titrated with KOH in the iso-propanol, the potential jumps at the TEP amounted 287 mV/0.3 mL (262 mV/0.3 mL with a glass electrode). While titrating α-nitroso-β-naphthol (a very weak acid, pK_a in water amounting to 7.77) with D_2/Pd as the sensor, the potential jumps at the TEP in iso-propanol amounted to 234 mV/0.3 mL (219 mV/0.3 mL with a glass electrode).

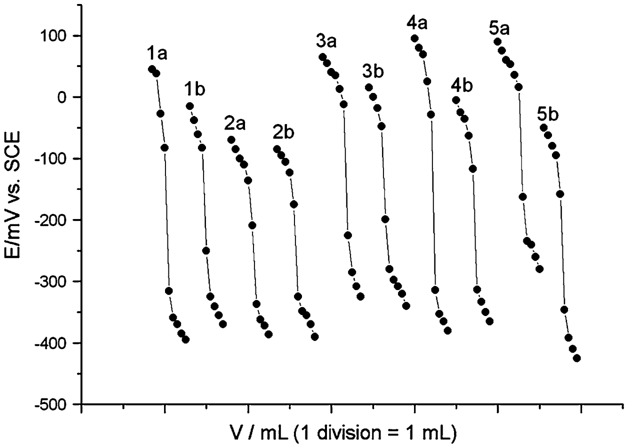

Fig. 5 The effect of the indicator electrode on the shape of the end-point inflexion in the potentiometric titration of stearic acid (1,3) and α-Nitroso-β-naphthol (2) and benzoic acid (4,5) in iso-propanol: 1a, 2a, 3a, 4a, 5a: D_2/Pd electrode; 1b, 2b, 3b, 4b, 5b: glass electrode. Titrant: 3a, 3b, 5a, 5b: KOH; 1a, 1b, 2a, 2b, 4a, 4b: TBAH

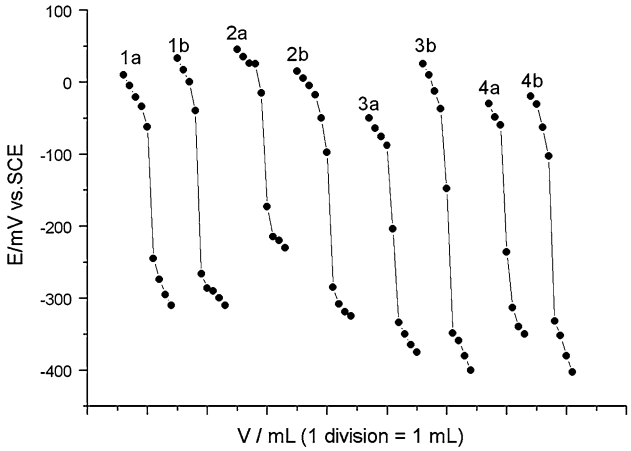

Fig. 6 The effect of the indicator electrode on the shape of the end-point inflexion in the potentiometric titration of benzoic acid (1,2) and stearic acid (3,4) in *tert*-butanol: 1a, 2a, 3a, 4a: D_2/Pd electrode; 1b, 2b, 3b, 4b: glass electrode. Titrant: 1a, 1b, 3a, 3b: KOH; 2a, 2b, 4a, 4b: TBAH

As can be seen in Table 1, when the D_2/Pd electrode was applied as the sensor, the potential jumps were either similar or higher than the jumps obtained when a glass electrode was used. The sensor (D_2) carrier is metallic palladium that is chemically inert in alcohols as solvent.

When the D_2/Pd electrode was applied as an indicator electrode in *tert*-butanol and iso-propanol as solvent, the potentials during the titration and at the equivalence point (TEP) were rapidly established (within a couple of minutes) and the change of the potential at the TEP coincided with the change of the applied indicator color.

Water slightly lowered the potential jumps at the TEP in the applied solvents. A more significant decrease of the potential jump was obtained when the content of water was increased by 10%.

The results obtained in the determination of the investigated acids (Table 2) in the investigated solvents using a D_2/Pd indicator electrode deviated on average by 0.01–0.35% from those obtained with a glass electrode.

Table 1 Potential jumps (mV/0.3 mL) at the end-point in the potentiometric titration of weak of acids in non-aqueous media

Solution	Titrated compound	Titrating agent	D_2/Pd-SCE	Glass-SCE
Iso-propanol	Benzoic acid	Potassium hydroxide	270	297
	Benzoic acid	TBAH	379	270
	Stearic acid	Potassium hydroxide	287	262
	Stearic acid	TBAH	324	265
	α-Nitroso-β-naphthol	TBAH	234	219
tert-butanol	Stearic acid	Potassium hydroxide	254	322
	Stearic acid	TBAH	303	291
	Benzoic acid	Potassium hydroxide	242	286
	Benzoic acid	TBAH	220	258

Table 2 Potentiometric titration of acids in iso-propanol and *tert*-butanol by the application of the electrode pair D_2/Pd-SCE and glass-SCE

Titrated acid	Solvent	No. of determ.	Taken mg	Found (%)	
				Glass-SCE	D_2/Pd-SCE
Benzoic acid	Iso-propanol	6	23.30	99.65 ± 0.28	99.98 ± 0.25[a]
Benzoic acid	Iso-propanol	6	23.30	99.88 ± 0.31	99.90 ± 0.30[b]
Stearic acid	Iso-propanol	5	68.75	97.65 ± 0.25	97.60 ± 0.28[a]
Stearic acid	Iso-propanol	6	68.75	97.75 ± 0.28	97.65 ± 0.30[b]
α-Nitroso-β-naphthol	Iso-propanol	7	45.40	97.99 ± 0.38	98.15 ± 0.40[b]
Stearic acid	*tert*-Butanol	6	66.25	97.65 ± 0.30	97.70 ± 0.28[a]
Stearic acid	*tert*-Butanol	5	66.25	97.60 ± 0.27	97.83 ± 0.27[b]
Benzoic acid	*tert*-Butanol	6	25.31	99.98 ± 0.25	99.85 ± 021[a]
Benzoic acid	*tert*-Butanol	6	25.31	99.82 ± 0.22	99.83 ± 0.31[b]

[a] Potassium hydroxide

[b] TBAH

Thus, it can be concluded that a D_2/Pd electrode can completely replace a glass electrode in the titration of acids in these solvents.

4 Conclusion

The obtained results show that a D_2/Pd electrode can be successfully applied as an indicator electrode for the titration of weak acids in *tert*-butanol and iso-propanol with standard base solutions (KOH and TBAH). The rapid establishment of the equilibrium potentials in the course of the titration, the sufficiently high potential jumps at the equivalence point, the rapid response, ease of preparation, small size, low cost, great hardiness, and chemical inertness to the working medium make this electrode very suitable for potentiometric titrations in the investigated alcohols.

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