VERSITA

Cent. Eur. J. Chem. • 7(4) • 2009 • 900–908
DOI: 10.2478/s11532-009-0074-3

Central European Journal of **Chemistry**

Use of the sulfide minerals pyrite and chalcopyrite as electrochemical sensors in non-aqueous solutions. The potentiometric titration of weak acids in alcohols

Research Article

Ljiljana Mihajlović[1], Snežana Nikolić-Mandić[2], Branislav Vukanović[3], Ranđel Mihajlović[1]*

[1] *Department of Chemistry, Faculty of Sciences, University of Kragujevac, 34 000 Kragujevac, Serbia*

[2] *Faculty of Chemistry, University of Belgrade, 11 000 Belgrade, Serbia*

[3] *Technical High School, 37000 Kruševac, Serbia*

Received 24 February 2009; Accepted 19 June 2009

Abstract: Natural monocrystalline pyrite and chalcopyrite were examined as new indicator electrodes for the potentiometric titration of weak acids in *tert*-butanol and *iso*-propanol. The electrodes investigated demonstrated a linear dynamic response for *p*-toluenesulfonic acid concentrations in the range from 0.1 to 0.001 M, with a Nernstian slope of 48 mV per decade for pyrite in *tert*-butanol. Sodium methylate, potassium hydroxide and tetrabutylammonium hydroxide (TBAH) proved to be suitable titrating agents. The response time was less than 12 s and the lifetime of the electrodes was higher than 1 year. The advantages of the electrodes are long-term stability, rapid response, reproducibility, easy preparation and low cost.

Keywords: *Pyrite • Chacopyrite • Sensor • Non-aqueous media • Alcohols*

1. Introduction

The end point cannot be titrated in water for chemicals of weakly acidic character when p*K* + p*c* (where *c* is the acid concentration) is greater than 8 because the pH change at the equivalence point in aqueous solution cannot be evaluated with reasonable accuracy. Moreover, most of these compounds are insoluble in water. Usually, these problems can be resolved partially or entirely by using an appropriate non-aqueous solvent as the reaction medium. Among non-aqueous solvents, alcohols (particularly *tert*-butanol and 2-propanol) were often used as the medium in numerous investigations. These alcohols are relatively inexpensive, have a great capacity to dissolve organic compounds with large molecular masses and their vapors have a comparatively low level of toxicity. They are particularly suitable as media in the application of instrumental methods, such as potentiometry, conductimetry, spectrophotometry, chromatography, *etc*., as well as in the application as indicators for the demonstration of titration end points. They are characterized by an enormous differentiating capacity (particularly *tert*-butanol and 2-propanol) in relation to acids and phenols and they are readily miscible with other organic solvents, which makes them suitable for application in analytical practice.

Tert-butanol is a differentiating solvent with a very small autoprotolysis constant (pK_s 22.13) [1] and a

* *E-mail: randjel@kg.ac.rs*

high relative acidity scale E_s (1100 mV) [2]. Therefore, it is very useful for the titration of weak acids with tetrabutylamonium hydroxide (TBAH) [3] and for differentiating the titration of carboxylic acids and phenol [4-6]. Due to its excellent solvent characteristics, fundamental information on acid-base equilibria would be very useful [7-13]. In this solvent, Fritz and Gainer coulometrically titrated mineral acids, sulfonic acids, carboxylic acids, enols, imides and phenols with electrically generated TBAH [14] and with visual and potentiometric determination of the titration end point (TEP).

Iso-propyl alcohol (also *iso*-propanol, 2-propanol), like *tert*-butanol, is a differentiating solvent with a low autoprotolysis constant (pK_s 21.08 [1], 21.1 [15]), a high relative acidity scale E_s (980 mV) [2] and a relative permittivity value of 19.9 [15]. Therefore, like *tert*-butyl alcohol, *iso*-propyl alcohol is a very useful solvent for the titration of weak acids [3,12], for the determination of many organic compounds [4,9,16-19], for the determination of pK_a values of azlactone dyes [8] and for the potentiometric titration of some hydroxylated benzoic acids and cinnamic acids [20] using TBAH under a nitrogen atmosphere at 25°C. Aktaş *et al*. [21] conductimetrically and potentiometrically titrated hydroxycinnamic acids using triethylamine and TBAH. Hine *et al*. [22] determined the relative acidity of five indicators in a solution of *iso*-propyl alcohol; Yalçin *et al*. [23] determined the pK_a values of 6-semicarbazone-9-17 mono methyl substituted octadecanoic acids using the potentiometric titration method. Gündüz *et al*. [24] potentiometrically titrated symmetric aliphatic dicarboxylic acids and selected binary mixtures. Bosch *et al*. [25] conductimetrically determined the dissociation constants of some anti-inflammatory agents in *iso*-propyl alcohol. Canel *et al*. [26] conductimetrically and potentiometrically investigated the effect of solvents and titrant on the formation of homoconjugates and concluded that the occurrence of homoconjugation was low in this solvent. Andrés and Romero [27] determined the acidic groups of fulvic acid from lignite by potentiometric titration in this solvent. Johansson [28] titrated very weak acids with 100% current efficiency in this solvent using a coulometrically generated base, while Cooksey *et al*. [29] generated the base stoichiometrically in tetraethylammonium bromide by reduction of the solvent, oxygen and traces of water. Saraç *et al.* [30] potentiometrically determined the molecular weight of a polymer. Özeroglu *et al.* potentiometrically and conductimetrically determined para and nitro substituted aromatic acids and dicarbonic acids in non-aqueous solvents [31,32] .

The literature demonstrates that *tert*-butanol and *iso*-propanol are extensively used as media for 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 non-aqueous media, these electrodes show certain undesirable features, *e.g.*, the potential response of a glass electrode in non-aqueous solutions 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. In the basic pH range, a glass electrode exhibits an alkaline error in non-aqueous solution [33].

These disadvantages of glass electrodes - high resistance, brittleness, contamination of the membrane, alkaline error, dehydration of the glass membrane in non-aqueous media - have led to intensive research for alternative pH electrodes in nonaqueous solutions. For this purpose, Greenhow and Al-Mudarris [34] used metal and metalloid indicator electrodes for the potentiometric titration of weak acids in dimethylformamide and 4-methyl-2-pentanone, Lintner *et al*. [35] used a platinum electrode for titration in tetrahydrofuran and Izutsu *et al*. [36-38] used a silicone nitride (Si_3N_4), tantalum oxide (Ta_2O_5) and iridium oxide pH sensor in non-aqueous solution.

In a previous study, 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 by the use of natural monocrystalline pyrite, chalcopyrite and galena as the electrochemical sensor for the potentiometric titration of weak acids in pyridine, pyrrolidone, N,N-dimethylformamide, propylene carbonate, γ-butyrolactone and nitriles [39-42]. Because alcohols (*tert*-butanol, *iso*-propanol) are very useful solvents, they have been extensively used as the medium in potentiometric determinations of many acidic substances. Therefore, in this study, the possibility of the application of pyrite and chalcopyrite as electrochemical sensors for the potentiometric titrations of weak acids in these solvents was investigated.

2. Experimental

2.1. Reagents and chemicals

All the chemicals used in the present study were of analytical reagent grade from Merck, Fluka, J.T.Baker or Karlo Erba. *Tert*-butanol and *iso*-propanol (Fluka) were *puriss* p.a. purity: *tert*-butanol (≥99.7%), used in this study had a water content ≤ 0.01%, and *iso*-propanol (≥99.8%) had a water content ≤ 0.1%. These solvents were used without further purification. The water content

in the solvents used was measured by Karl Fischer titration.

Solutions of the acids (*α*-nitroso-*β*-naphthol (Merck), benzoic acid (Merck), and stearic acid (Karlo Erba)) were prepared by weighing a specific amount of the acid and dissolving it in the titration solvent. The concentrations of the acid solutions were controlled by titration with standard 0.1 M Bu_4NOH (TBAH) using visual end-point detection or potentiometric end-point detection by means of a glass electrode-modified SCE (saturated calomel electrode) couple. *p*-Toluenesulfonic acid (Karlo Erba) monohydrate was dried under vacuum over P_2O_5 at 70 – 80°C for several days.

A solution of sodium methylate in a mixture of benzene and methanol was prepared according to Kreshkov *et al*. [43]. This solution was standardized by titration against benzoic acid dissolved in benzene/methanol. Although the reagent is reasonably stable, it was restandardized every few days.

Laboratory reagent grade TBAH (0.1 M) in *iso*-propanol-methanol (10:1 v/v) (Fluka) was standardized against benzoic acid using Thymol Blue as the indicator. The Thymol Blue indicator solution was prepared by dissolving 0.1 g Thymol Blue in 100 mL of methanol. Laboratory reagent grade potassium hydroxide (0.1 M) in ethanol (Riedel-de Haën) was standardized against benzoic acid using Thymol Blue as the indicator. The required volume of the acid was measured by means of a micro-burette with a PTFE stopcock; 2 – 3 mL of the acids investigated was used. All measurements were performed at room temperature between 20 and 25°C, with the exception of measurements using *tert*-butanol which were performed at 28°C.

2.2. Electrodes

Indicator electrodes formed from pyrite and chalcopyrite were described in previous papers [39-42]. These sensors should not be kept in the solvents prior to titration. The experiments were performed with either a sample of natural pyrite or a chalcopyrite crystal from the Veliki Krivelj copper mine (Bor, Serbia).

The responses of the pyrite and chalcopyrite indicator electrodes in alcohols were compared with that of a conventional glass electrode type G-202C (Radiometer, Copenhagen). The glass electrode was conditioned in the appropriate solvent before use.

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

2.3. Apparatus

The apparatus employed to follow the potential changes of the pyrite and chalcopyrite electrodes with time and for end-point detection with a pyrite electrode-SCE, chalcopyrite-SCE, or a glass electrode-SCE couple, was described in previous publications [41-42]. The potential changes during the titration were followed with a pH-meter model MV 870 DIGITAL-pH-MESSEGERÄT, Praectronic, Dresden, Germany. The same apparatus with an additional temperature-controlled cell was used to follow the potential changes of the 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 pyrite and chalcopyrite electrodes were performed in a series of *p*-toluenesulfonic acid solutions in the concentration range of 0.1 – 0.001 mol L^{-1}. Changes in the potential of these electrodes over time were followed in a temperature-controlled cell (25±0.1°C and 28±0.1°C). The ionic strength of the solution was maintained with 0.05 M tetrabutylammonium perchlorate. The change of the potential of the pyrite and chalcopyrite electrodes with time was followed in the required solvent. The potential values determined in this manner were used to calculate the slopes of the lines of potential *versus* time. This indicator electrode was coupled with a modified SCE as the reference electrode.

2.4.2 Potentiometric titration

The required solvent (10 mL), which was previously titrated, was placed in the titration vessel and a measured volume of the acid under investigation and two drops of indicator solution were added. The indicator electrode, either the pyrite, chacopyrite or glass electrode, and a modified calomel reference electrode 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 M TBAH, potassium hydroxide or sodium methylate. The potential was measured after each addition of the titrant. The potential measurements were performed at 2-min intervals during the course of the titration. The titration end-points were determined from the second derivative by the classical method.

3. Results and Discussion

3.1. Mechanism

The potential of a pyrite electrode in water [44], N,N-dimethylformamide, methylpyrrolidone, pyridine and nitriles [40-42], and the potential of a chalcopyrite

electrode in *γ*-butyrolactone, propylene carbonate, N,N-dimethylformamide and methylpyrrolidone [40,41], were reported in the literature to depend on the activity of H_3O^+ ions according to Eq. 1:

$$E = E^{o}_{ox} + \frac{RT}{nF} \ln a^{k}_{H_3O^+} \quad (1)$$

This equation can also be applied in alcohols containing a weak organic acid.

If an ISE (ion selective electrode) is to be applied as a sensor for quantitative measurements in a non-aqueous environment, various conditions should be fulfilled. A stable potential in acid and base medium, an adequate slope and sensitivity, a short response time, a long lifetime and repeatability are necessary for successful operation.

3.2. Potential of the pyrite and chalcopyrite electrodes

The stationary potentials of the pyrite and chalcopyrite electrodes in *tert*-butanol and *iso*-propanol were measured by direct potentiometry at 25 ± 0.1°C and at 28 ± 0.1°C in a freshly prepared 0.05 M solution of *p*-toluenesulfonic acid or stearic acid in the appropriate solvent. All measurements were performed in the presence of a background electrolyte of constant ionic strength (0.05 M tetrabutylammonium perchlorate). In all of the solutions investigated, a stable potential (for both electrodes in all alcohols) was attained in less than 4 – 5 min.

3.3. Slope of the potential response of the pyrite and chalcopyrite electrodes

The potential of the pyrite and chalcopyrite electrodes was measured using a series of concentrations of *p*-toluenesulfonic acid in the range of 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 M with tetrabutylammonium perchlorate. The values of the slopes of the potential in *tert*-butanol were 48 mV per decade for the range of concentrations tested (Fig. 1). Similar slopes were obtained for *iso*-propanol. Because the pyrite and chalcopyrite electrode exhibit sub-Nernstian dependences, they cannot be used for the measurement of the pH of a solution. However, the potentials of these electrodes are very stable with respect to time; hence, they can be successfully applied for the titrations of acids in *tert*-butanol and *iso*-propanol as solvents.

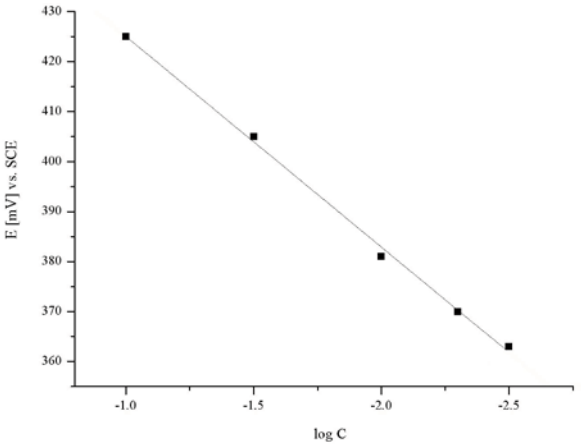

Figure 1. Plots of the pyrite electrode potential *vs.* log c (p-toluenesulfonic acid) in tert-butanol.

3.4. Response time of the electrodes

The response time of the electrodes was determined by recording the time elapsed before a stable potential value was attained after the pyrite, or the chalcopyrite electrode and the reference electrode (modified SCE) were immersed in the calibration solutions. The calibration solutions were varied from a highly acidic solution (0.05 M *p*-toluenesulfonic acid) to a highly basic solution (0.05 M TBAH). From the acidic (*p*-toluenesulfonic acid) to the basic region (TBAH), the change of the electrode potential for the pyrite electrode ranged from + 429 mV to – 348 mV (*iso*-propanol) and for the chalcopyrite electrode ranged from + 436 mV to – 101 mV (*iso*-propanol). Therefore, the potential changes at the TEP (titration end point) for the pyrite electrode were greater than those for the chalcopyrite electrode (Table 1). The response time for the pyrite electrode was 11 s and for the chalcopyrite electrode was 12 s in the alcohols examined. These results are within the limits of the results obtained by many hydrogen electrodes giving a linear response within the same pH range. In conclusion, the response times of the pyrite and chalcopyrite electrodes prepared in this research were comparable to similar electrodes reported in the literature [45,46].

3.5. Lifetime and repeatability

The lifetime of the electrodes was determined by increasing the potential values of the calibration solution (*p*-toluenesulfonic acid) and plotting the calibration curves for a period of 1 year. The slope of electrode potential *vs.* log c remained constant. However, if the electrode was used frequently and for a long time, it was necessary to rub the pyrite or chalcopyrite crystals with aluminum oxide and wash the electrode before continuing use.

Table 1. Changes in potential (mV/0.3 mL) at the end-point in the potentiometric titration of weak of acids in alcohols

Solvent	Titrated acid	Titrating agent	FeS_2-SCE	$CuFeS_2$-SCE	Glass-SCE
Iso-propanol	Stearic acid	KOH	235	132	262
	Stearic acid	TBAH	196	127	265
	α-Nitroso-β-naphtol	TBAH	197	77	219
	Benzoic acid	Sodium methylate	317		
	Benzoic acid	KOH	230		297
	Benzoic acid	TBAH	198		270
tert-butanol	Stearic acid	KOH	219		322
	Stearic acid	TBAH	130		291
	Benzoic acid	KOH	168	182	286
	Benzoic acid	TBAH	107	76	258

In order to establish the efficiency of use of the pyrite and chalcopyrite electrodes in potentiometric titrations and the repeatability of the obtained results, the titration of stearic acid with TBAH was selected as a model. The titration was performed repetitively five times and the end point was monitored using these electrodes. The titration curves obtained in the titration of stearic acid with TBAH are illustrated in Fig. 2. The titration end-points were determined from the second derivative by the classical method (Fig. 3). The relative standard deviation (RSD) for the end point determination of the titration was 0.31%. The values of the RSD for the end-point determination of the titrations of different acids ranged from 0.23 to 0.42% (Tables 2 and 3).

3.6. Analytical application. Titration of acids in tert-butanol, iso-propanol and iso-amyl alcohol

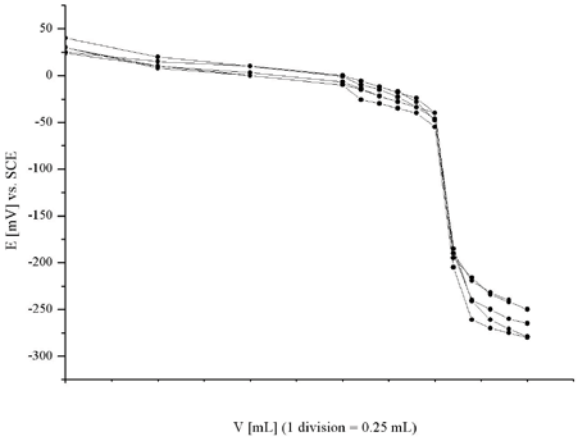

Figure 2. Five titration curves for 2 mL of stearic acid solution (●0.09 M), by a standard TBAH solution of 0.1 M, using pyrite as an indicator electrode in iso-propanol.

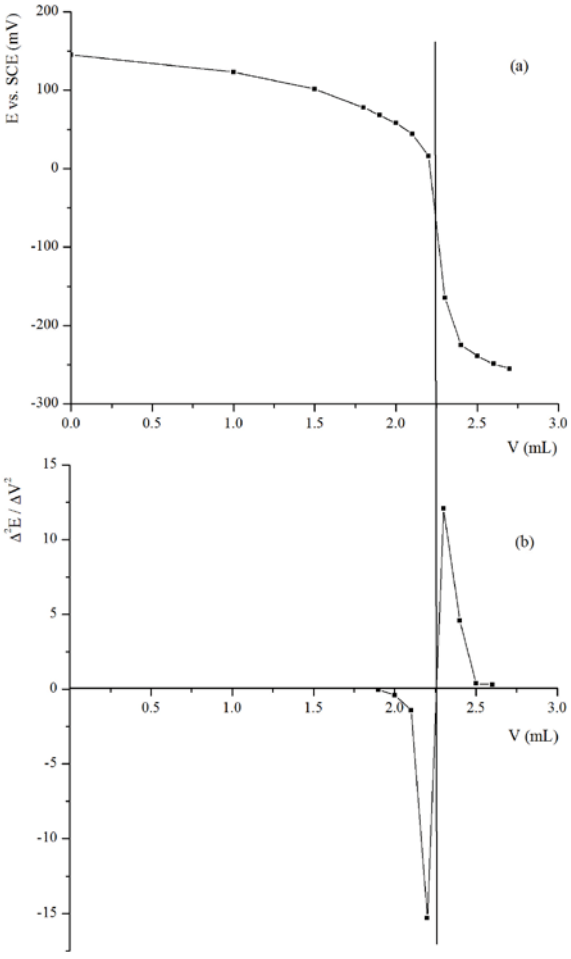

Figure 3. Potentiometric titration of 2 mL stearic acid solution (■0.09 M) by standard 0.1 M TBAH using pyrite as an indicator electrode: (a) titration curve; (b) second-derivative curve.

Table 2. Potentiometric titration of acids in iso-propanol by the application of the electrode pair Pyrite-SCE and glass-SCE.

Titrated acid	Solvent	No.of determ.	Taken mg of acid	Found (%)	
				Glass-SCE	Pyrite-SCE
Benzoic acid	Iso-propanol	6	23,30	99.90±0.26	99.92±0.27[a]
Benzoic acid	Iso-propanol	6	23.30	99.65±0.28	99.90±0.26[b]
Benzoic acid	Iso-propanol	6	23.30	99.88±0.31	99.89±0.33[c]
Stearic acid	Iso-propanol	6	68.75	97,65±0,25	97,50±0,26[b]
Stearic acid	Iso-propanol	5	68.75	97,75±0,28	97,60±0,31[c]
α-Nitroso-β-naphthol	Iso-propanol	7	45.40	97.99±0.38	98.05±0.42[c]
Stearic acid	tert-butanol	6	66.25	97,65±0,30	97,80±0,38[b]
Stearic acid	tert-butanol	5	66.25	97,60±0,27	97,66±0,41[c]
Benzoic acid	tert-butanol	6	25.31	99.98±0.25	99.88±023[b]
Benzoic acid	tert-butanol	6	25.31	99.82±0.22	99.83±0.31[c]

[a]*Sodium methylate*
[b]*Potassium hydroxide*
[c]*TBAH*

Table 3. Potentiometric titration of acids in iso-propanol by the application of the electrode pair chalcopyrite-SCE and glass-SCE.

Titrated acid	Solvent	No.of determ.	Taken mg of acid	Observed (%)	
				Glass-SCE	Chalcopyrite –SCE
Stearic acid	Iso-propanol	6	68.65	97.65±0.25	97.30±0.24[b]
Stearic acid	Iso-propanol	6	68.65	97.75±0.28	97.50±0.33[c]
α-Nitroso-β-naphthol	Iso-propanol	6	45.40	97.99±0.38	97.58±0.41[c]
Benzoic acid	tert-butanol	5	25.31	99.98±0.25	99.82±025[b]
Benzoic acid	tert-butanol	7	25.31	99.82±0.22	99.62±0.28[c]

[b] *Potassium hydroxide*
[c]*TBAH*

TBAH, potassium hydroxide and sodium methylate are most often used as the titrant for the titration of acidic substances in alcoholic solvents with a glass electrode as the indicator. In this study, because the new sensors pyrite and chalcopyrite are proposed instead of a glass electrode in the determination of the TEP, in addition to TBAH, sodium methylate and KOH in anhydrous methanol were used as the titrations means in all the present investigations.

The practical utility of the proposed sensors was tested by their employment as indicator electrodes for the titration of weak acids of different strengths, *i.e.*, benzoic acid (pK_a in water is 4.20), stearic acid (pK_a in water is 5.0) and *α*-nitroso-*β*-naphthol (pK_a in water is 7.77), with methanolic potassium hydroxide, TBAH or sodium methylate solutions.

The titration of an acid, for example in *iso*-propanol, with sodium methylate, TBAH, or KOH, can be represented by Eqs. 2-4, respectively:

$$HA + CH_3ONa \rightarrow NaA + CH_3OH \quad (2)$$

$$R_4NOH + HA \rightarrow R_4NA + H_2O \quad (3)$$

$$HA + KOH \rightarrow KA + H_2O \quad (4)$$

The neutralization reactions can be expressed in an analogous manner in *tert*-butanol.

Water, generated in the reactions depicted in Eqs. 3 and 4, has a negative effect on the titration of acids with KOH and TBAH. In dilute aqueous solutions, the activity of the water would be constant, but if the Nernst equation is applied in non-aqueous solution (in alcohols), the potential would be related to the activities of both the hydrogen ions and water according to Eq. 5.

$$E = E^o + \frac{RT}{nF} \ln \frac{a^k_{H_3O^+}}{(a_{H_3O})^{2k}} \quad (5)$$

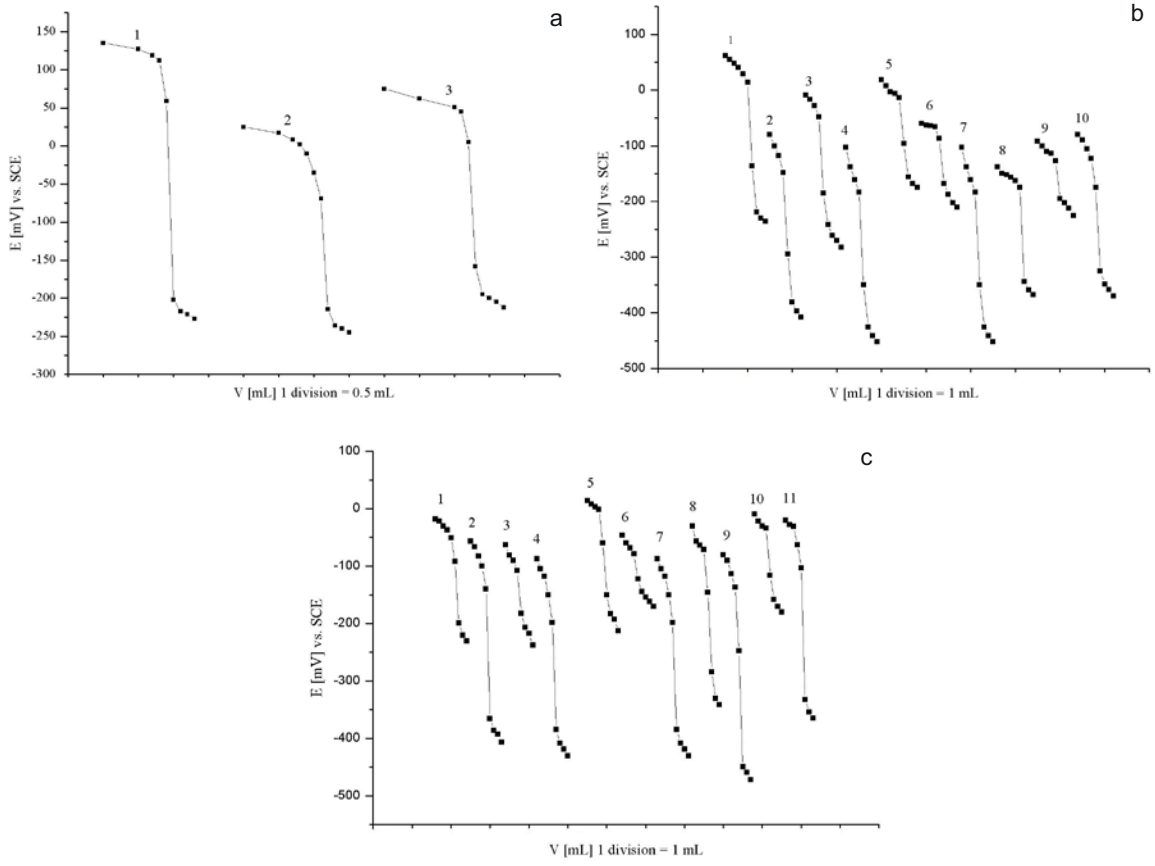

Figure 4. (a) The effect of the indicator electrode on the shape of the end-point inflexion in the potentiometric titration of benzoic acid in iso-propanol using the following titrants: (1) sodium methylate, (2) TBAH, and (3) KOH;
(b) the effect of the indicator electrode on the shape of the end-point inflexion in the potentiometric titration of (1-7) stearic acid and (8-10) α-Nitroso-β-naphthol in iso-propanol using the following electrodes: (1), (3), and (8) pyrite; (5), (6), and (9) chalcopyrite; and (2), (4), (7), and (10) glass; and the following titrants: (1), (2), and (5) KOH; and (3), (4), and (6 -10) TBAH;
(c) the effect of the indicator electrode on the shape of the end-point inflexion in the potentiometric titration of (1-7) benzoic acid and (8-11) stearic acid in tert-butanol using the following electrodes: (1), (3), (8), and (10) pyrite; (5) and (6) chalcopyrite; and (2), (4), (7), (9), and (11) glass, and the following titrants: (1), (2), (5), (8), and (9) KOH; and (3), (4), (6), (7), (10), and (11) TBAH.

The titration curves of benzoic acid in *iso*-propanol as the solvent with sodium methylate, potassium hydroxide or TBAH as titrants, using the electrode couple pyrite-SCE, are illustrated in Fig. 4a. The titration curves of benzoic acid, stearic acid and *α*-nitroso-*β*-naphthol in *tert*-butanol or *iso*-propanol as solvents, and with potassium hydroxide or TBAH as titrants, using the electrode couples pyrite-SCE, chalcopyrite-SCE and glass-SCE are illustrated in Figs. 4b and c, respectively. The changes in potential (mV/0.3 mL) at the end-point in the potentiometric titration of weak acids in alcohol are listed in Table 1. The greatest change in potential at the TEP (317 mV/0.3 mL) was obtained for the titration of benzoic acid in *iso*-propanol, using sodium methylate as the titrant and pyrite as the sensor. Using the same sensor in the same solvent, the changes in the potential when benzoic acid was titrated with KOH and TBAH were 235 mV/0.3 mL and 196 mV/0.3 mL, respectively. In the titration of benzoic acid using a glass electrode as the indicator, the changes in the potential at the TEP with KOH and TBAH were 262 and 265 mV/0.3 mL, respectively. When a glass electrode was used for TEP detection, the change in the potential was barely perceptible when sodium methylate was applied as the titrant, due to the effect of sodium ions on the glass electrode. Similar changes in the potential were obtained for the titrations of stearic and benzoic acids in *tert*-butanol (Table 1).

When benzoic acid, stearic acid and *α*-nitroso-*β*-naphthol were titrated with KOH or TBAH as the titrants in the same solvent but with chalcopyrite as the sensor, the changes in the potential at the TEP were half as large as those obtained with pyrite as the sensor. Although the changes in the potential obtained with TBAH or KOH

and the chalcopyrite sensors are lower than for the pyrite sensor, they are distinctive enough to allow the precise determination of the TEP in the titration of very weak acids.

The changes in the potential which were obtained in the titration of weak acids with sodium methylate, KOH or TBAH in alcohols using pyrite as a sensor are similar to the changes obtained in the titration of these acids in N,N-dimethylformamide, methylpyrrolidone, and nitriles (39,42). If chalcopyrite is used as a sensor in the titration of weak acids in N,N-dimethylformamide and methylpyrrolidone, the changes in the potential are somewhat lower. In the titration of the same acids in alcohols, *γ*-butyrolactone and propylene carbonate using chalcopyrite as a sensor, the changes in the potential were nearly 50% lower than the data observed for pyrite as a sensor, but were great enough for accurate determination of the TEP (greater than 60 mV). The results are in accordance with the physical-chemical properties of the solvents including relative permittivity, basicity of the solvent, differentiating capacity and widely ranging acidity. In addition, all of the titrants (KOH, TBAH, and sodium methylate) can be applied in alcohols, nitriles, N,N-dimethylformamide and N-methylpirolidone, while only KOH was appropriate for use in *γ*-butirolaktone and propilene carbonate.

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

The presence of water slightly lowered the change in the potential at the TEP in the applied solvents. The impact of water on the decrease of the potential was greater in the titration of the very weak acid. Because water is released during the titration of acids when applying TBAH or KOH, sodium methylate should be used as the titrant in such cases. A more significant decrease of the change in the potential was obtained when the content of water was increased by 10%.

The results obtained in the determination of the acids, solvents, and indicator electrodes investigated in this research (Tables 2 and 3) deviated on average by 0.01 – 0.41% from those obtained with a glass electrode. Therefore, it was concluded that the electrodes examined in this research can replace a glass electrode in the titration of acids in the solvents tested.

4. Conclusions

The results demonstrated that natural monocrystalline pyrite can be successfully applied as an indicator electrode for the titration of weak acids in *tert*-butanol and *iso*-propanol with standard basic solutions (sodium methylate, KOH and TBAH). If natural monocrystalline chalcopyrite is used as the sensor, somewhat lower, but sufficiently large changes in the potential at the TEP were obtained in *tert*-butanol and *iso*-propanol. Variation in the potential during the course of the titrations and at the TEP were rapidly established. The sensors examined in this research are easy to prepare, inexpensive, robust, chemically inert in alcohols, and the lifetime of the electrode is sufficiently long.

Acknowledgment

This work was funded by the Ministry of Science and Technological Development of the Republic of Serbia (Project No. 142060B).

References

[1] A.P. Kreshkov, N.T. Smolova, T.J. Burmistrova, J. Phys. Chem. 50, 987 (1976)
[2] A.P. Kreshkov, Analytic Chemistry of Non-Aqueous Solution (Khimiya, Moscow, 1982) 187 (in Russian)
[3] A. Aslan, Y. Erdogan, A. Demirbaš, S. Karslioglu, Farmazie 52, 309 (1997)
[4] M. Alkan et al., Molecules 12, 1805 (2007)
[5] Ya.I. Korenman, T.N. Yermolaeva, Analyst 120, 2387 (1995)
[6] J.S. Fritz, L.W. Marple, Anal. Chem. 34, 921 (1962)
[7] I.M. Kolthoff, M.K. Chantooni, Jr., Anal. Chem. 50, 1440 (1978)
[8] K. Ertekin, S. Alp, I. Yalcin, Dyes and Pigments 65, 33 (2005)
[9] H. Yüksek, Z. Osak, M. Alkan, Ş. Bahçeci, M. Özdemir, Molecules 9, 232 (2004)
[10] L.W. Marple, G.J. Scheppers, Anal. Chem. 38, 553 (1966)

[11] L.W. Marple, J.S. Fritz, Anal. Chem. 35, 1223 (1963)
[12] L.W. Marple, J.S. Fritz, Anal. Chem. 34, 796 (1962)
[13] E. Bosch, C. Rodés, M. Rosés, Electroanalysis 3, 365 (1991)
[14] J.S. Fritz, F.E. Gainer, Talanta 15, 939 (1968)
[15] K. Izutsu, Electrochemistry in Nonaqueous Solution (Wiley-VCS, Germany, 2002)
[16] H. Yüksek et al., Asian J. Chem. 17, 195, (2005)
[17] H. Yksek, M. Alkan, Ş. Bahçeci, Molbank M462 (2006)
[18] Ş. Bahçeci, H. Yüksek, Z. Ocak, C. Köksal, M. Özdemir, Acta Chim. Slov. 49, 783 (2002)
[19] Ş. Bahçeci, H. Yüksek, Z. Ocak, I. Azakli, M. Özdemir, Collect. Czech. Chem. Commun. 67, 1215 (2002)
[20] A.A. Hakan, Y. Samin, Acta Chim. Slov. 51, 273 (2004)
[21] A.H. Aktaş, G. Yaşar, G.Ö. Alsancak, Ş. Demirci, Turk. J. Chem. 25, 501 (2001)
[22] J. Hine, M. Hine, J. Am. Chem. Soc. 74, 5266 (1952)
[23] M. Yalçin, S. Tanyolaç I. Kizilcikli, A. Tavman, Turk. J. Chem. 22, 155 (1998)
[24] T. Gündüz, E. Kiliç G. Özkan, Analyst 113, 1017 (1988)
[25] E. Bosch, C. Rodés, M. Rosés, Electroanalysis 3, 365 (1991)
[26] E. Canel, M. Taştekin, O. Atakol, E. Kiliç, Turk. J. Chem. 27, 77 (2003)
[27] J.M. Andrés, C. Romero, Fuel 67, 1305 (1988)
[28] G. Johansson, Talanta 11, 789 (1964)
[29] B.G. Cooksey, B. Metters, J.M. Ottaway, D.W. Whymark, Talanta 20, 371 (1973)
[30] A.S. Saraç, B. Ustamehmetoglu, C. Erbil, Polym Bulletin 32, 91 (1994)
[31] C. Özeroglu, H. Cankurtaran, Indian Journal Chem. 40B, 438 (2001)
[32] C. Özeroglu, A.S. Saraç, Asian J. Chem. 18(3), 1808 (2006)
[33] B. Karlberg, G. Johansson, Talanta 16, 1545 (1969)
[34] E.J. Greenhow, B.F. Al-Mudarris, Talanta 22, 417 (1975)
[35] C.J. Lintner, R.H. Schleif, T. Higuchi, Anal. Chem. 22, 534 (1950)
[36] K. Izutsu, T. Nakamura, T. Arai, M. Ohmaki, Electroanalysis 7, 884 (1955)
[37] K. Izutsu, M. Ohmaki, Talanta 43, 643 (1996)
[38] K. Izutsu, H. Yamamoto, Anal. Sci. 12, 905 (1996)
[39] Lj.V. Mihajlović, R.P. Mihajlović, M.M. Antonijević, B.V. Vukanović, Talanta 64, 879 (2004)
[40] R.P. Mihajlović, Z.D. Stanić, J. Solid State Electrochem. 9, 558 (2005)
[41] Lj.V. Mihajlović, S.D. Nikolić-Mandić, B.V. Vukanović, R.P. Mihajlović, J. Solid State Electrochem. 13, 895 (2009)
[42] Lj. Mihajlović, S. Nikolić-Mandić, B. Vukanović, R. Mihajlović, Anal. Sci. 25, 437 (2009)
[43] A.P. Kreshkov, L.N. Bykova, N.A. Kazaryan, Kislotno-osnovnoe titrovanie v nevodnykh rastvorakh (Khimia, Moskow, 1967) (in Russian)
[44] M. Antonijević, B. Vukanović, R. Mihajlović, Talanta 39, 809 (1992)
[45] N. Oyama, T. Hirokawa, S. Yamaguchi, N. Ushizawa, T. Shimomura, Anal. Chem. 59, 258 (1987)
[46] D. Kuruoglu, E. Canel, Sh. Memon, M. Yilmaz, E. Kiliç, Anal. Sci. 19, 217 (2003)