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Randjel P. Mihajlović · Zorka D. Stanić

Natural monocrystalline chalcopyrite and galena as electrochemical sensors in non-aqueous solvents. Part I: potentiometric titrations of weak acids in γ-butyrolactone and propylene carbonate

Abstract Natural monocrystalline chalcopyrite and galena as new indicator electrodes for the potentiometric titrations of benzoic, anthranilic, α-nitroso-β-naphthol and salicylic acids in γ-butyrolactone (GBL) and propylene carbonate have been used. Potassium hydroxide in methanol was employed as the titrating agent. The results are compared with those obtained using a glass electrode. The investigated electrodes showed a linear dynamic response for p-toluensulfonic acid concentrations in the range from 0.1 to 0.001 M, with a Nernstian slope of 63 mV for chalcopyrite, 66 mV per decade for galena in GBL, 77 mV for chalcopyrite and 98 mV per decade for galena in propylene carbonate. Both electrodes showed a relatively fast response time and can be used without any time limit or without considerable divergence in potentials. The standard deviation of the determination of the investigated acids was less than 0.5%.

Keywords Chalcopyrite · Galena · Potentiometry · γ-Butyrolactone · Propylene carbonate

Introduction

During the past several decades, various indicator electrodes have been tested in non-aqueous dipolar aprotic solvents, such as γ-butyrolactone (GBL) and propylene carbonate (PC), and the results obtained showed that the electrodes respond under carefully controlled conditions in a manner useful for both fundamental and applied purposes [1].

R. P. Mihajlović (✉) · Z. D. Stanić
Department of Chemistry, Faculty of Sciences,
University of Kragujevac, R. Domanović 12,
P.O. Box 60, 34000 Kragujevac, Serbia Montenegro
E-mail: randjel@knez.uis.kg.ac.yu

The potentiometric titrations of acids using a glass electrode–saturated calomel electrode (SCE) as the electrode couple and tetrabutylammonium hydroxide, potassium hydroxide and sodium hydroxide as the titrating agents [2] and the behavior of a hydrogen electrode [3] in PC have been investigated. Acid–base equilibriums of some acids have also been examined in this solvent using a glass and $Ag/AgClO_4$ electrodes [4]. Coetzee and Martin [5] evaluated the response of a single-crystal lanthanum fluoride electrode in both direct potentiometry and potentiometric titrations in PC and in its mixture with water. Recently, potentiometric acid–base determinations in this solvent with antimony, anodically polarized platinum and preheated platinum electrodes have been carried out [6]. The H_2/Pd and D_2/Pd electrodes, both as the indicator electrode and the reference electrode, have been employed for the titration of different acids in propylene carbonate [7].

Coetzee et al. [8] reported the potentiometric characterization of the GBL using ion-selective electrodes. The dissociation constants of some acids and protonated bases in GBL have been determined and the obtained pK_a values were compared with those in PC [9]. The results obtained with an iridium oxide pH-sensor in GBL and PC solvents were compared with those obtained with a glass electrode and a pH-ISFETs [10].

Potentiometric sensors can offer an inexpensive and convenient method for the analyses of some weak acids in non-aqueous solutions. In order to make potentiometric titration in non-aqueous solutions easier and more reliable, it seemed reasonable to investigate new sensors for non-aqueous systems. Chalcopyrite and galena are sulfide minerals with the formula $CuFeS_2$ and PbS, respectively. The electrochemical behavior of chalcopyrite and galena under different current conditions has been intensively investigated [11–18]. Although galvanic interaction is a well-known phenomenon, the exact processes and mechanism of this effect are not thoroughly understood in sulfide mineral systems.

The mechanisms which lead to selective leaching in sulfide mineral system have been investigated in great detail [11]. It was found that the formation of a galvanic cell between electrically conducting minerals caused a suppression of the leaching of some sulfides. In order to quantify the galvanic interactions accurately, this consideration should be given to both the thermodynamics and the kinetics of electrode processes [11]. The presence of non-linear current–voltage characteristics at the mineral–mineral contacts in the galena–chalcopyrite and chalcopyrite–pyrite galvanic couples has been confirmed [12]. Additionally, it was found that the voltage loss across the mineral–mineral contacts may be of sufficient magnitude to affect the operation of the galvanic cell.

The anodic dissolution process of chalcopyrite using various auxiliary analytical methods for the identification of the reaction products [13–15] and the cathodic reduction of chalcopyrite [16] have been investigated by different authors. The voltammetry method was employed to investigate the electrochemical oxidation of a PbS rotating disk electrode and the results showed that the current was controlled by the rate of the electrochemical reaction [17]. The anodic and cathodic potential-dependent reaction of PbS in perchlorate medium by cyclic voltammetric studies on carbon paste medium electrodes–galena has been investigated [18].

Antonijević et al. [19] used natural monocrystalline chalcopyrite as the electrode material for the potentiometric titration of acids in water. However, the mentioned investigations did not encompass a study of the properties of galena sensors, although galena, being a semiconductor, may be expected to behave as an electrochemical sensor. It was found that the rate of oxidation of chalcopyrite and galena depends on the hydrogen ion concentration [20, 21], as well as on the concentration of other ionic species.

Considering all the above-mentioned findings, we considered that chalcopyrite and galena could be used as electrochemical sensors in non-aqueous solutions and, hence, it would be of interest to investigate the behavior of these electrodes in the potentiometric determination of some weak acids in GBL and PC.

Experimental

Reagents

All the chemicals used in the present study were of analytical reagent grade from either Merck or Fluka. γ-Butyrolactone and propylene carbonate (Fluka) were puriss p.a. purity (≥99%). These solvents were used without further purification.

Solutions of the acids were prepared by weighing a definite amount of an acid and dissolving it in titrated solvent. The concentrations of the solutions of the acids were controlled by titration with standard 0.1 M potassium hydroxide using visual end-point detection or potentiometric end-point detection by means of a glass electrode–modified SCE couple.

Methanolic potassium hydroxide was prepared according to Kreshkov [22]. The ionic strength of the solution was maintained with 0.1 M sodium perchlorate in propylene carbonate or GBL. A 0.10% solution of Thymol Blue in GBL and propylene carbonate was used as the indicator.

The required volumes of the acids were measured by means of a micro burette with a PTFE stopcock; 2.00 ml of the investigated acids were measured.

Apparatus and electrodes

The apparatus used to follow the potential changes of the chalcopyrite and galena electrodes with time and for end-point detection with either a chalcopyrite electrode–SCE, a galena 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.

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

The experiments were carried out with either a sample of natural chalcopyrite or a galena crystal from the Veliki Krivelj copper mine (Bor, Serbia) and the Stari Trg lead mine (K. Mitrovica, Serbia).

The indicator chalcopyrite electrode was prepared in the following manner: A quadratic piece of chalcopyrite
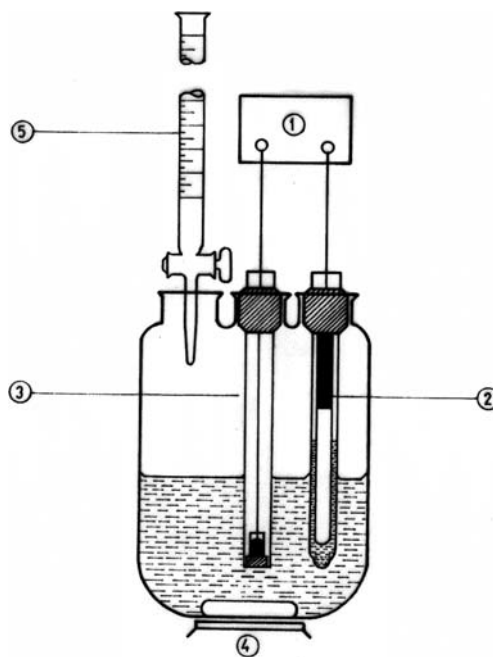

Fig. 1 Scheme of the apparatus for potentiometric titration of acids: (1) pH meter; (2) reference electrode; (3) indicator electrode (chalcopyrite or galena electrode); (4) magnetic stirrer; (5) burette

($a = 0.5$ cm) was used as the electrode material. The chalcopyrite electrode was made by polishing the chalcopyrite crystal with diamond paste, and the best polished side was used as the working surface of the electrode. A narrow glass tube was fixed with glue to the other side of the electrode and then filled with mercury. One end of a cupper wire was immersed in the mercury and this device was mounted into a wider glass tube ($\varnothing = 1$ cm) which was then cemented with a cold sealing mass based on methyl methacrylate. After solidification of this mass, the working surface of electrode was polished to a high glow. The electrode was then rinsed with distilled water and alcohol and dried in air after which it was ready for use. A galena indicator electrode was prepared in a similar way.

The response of the indicator chalcopyrite and galena electrodes in GBL and propylene carbonate was compared with that of a conventional glass electrode type G-202C (Radiometer, Copenhagen). The glass electrode was conditioned in the appropriate solvent for 48 h before use.

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

Procedures

Potential measurement

Stationary potential measurements of the chalcopyrite and galena electrodes were carried out in a series of p-toluensulfonic acid in the concentration range of 0.1–0.001 M. The potential of these electrodes with time was followed in a temperature-controlled cell (25 ± 0.1°C). The ionic strength of the solution was maintained with 0.1 M sodium perchlorate. The potential values determined in this way were used for the calculations of the slopes.

The change of the potential of the chalcopyrite and galena electrodes with time was followed in the required solvent. These indicator electrodes were coupled with a modified SCE as the reference electrode.

Potentiometric titration

A certain volume (10 ml) of the required solvent that 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 chalcopyrite or galena, or a glass electrode and a modified calomel electrode as the reference were immersed in the solution and connected to a pH meter. The potentiometric titration was then carried out by the addition of 0.1 M standard potassium hydroxide solution in aliquot of 0.05 ml, and the
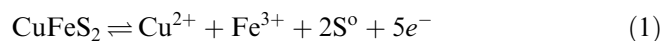
potential was read after each addition of the titrant. The potential measurements were made at 2-min intervals during the course of the titration. The titration endpoints were determined by the classical method from the second derivative.
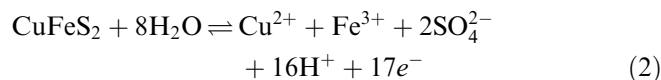
Results and discussion

The properties of the chalcopyrite mineral as conditions for the acid–base titrations in non-aqueous solutions

Chalcopyrite is a very unreactive mineral which is sparingly soluble in water. It is more intensely dissolved only in the presence of stronger oxidizing agents giving rise to different oxidation products (Cu^{2+}, Cu^+, Fe^{3+}, Fe^{2+}, S^o, SO_4^{2-}, $Cu(OH)^+$, $Fe(OH)^{2+}$, $Fe(OH)_3$, etc.), which depend on many factors (the nature of the oxidant, pH value, temperature, nature and concentration of present cations, anions and other chemical species, etc). The process of chalcopyrite oxidation is very complicated, but it could be described by the following equations:

Oxidation to elemental sulfur

$$CuFeS_2 \rightleftharpoons Cu^{2+} + Fe^{3+} + 2S^o + 5e^- \tag{1}$$

Oxidation to sulfate

$$CuFeS_2 + 8H_2O \rightleftharpoons Cu^{2+} + Fe^{3+} + 2SO_4^{2-} \\ + 16H^+ + 17e^- \tag{2}$$

As it can be seen from these equations, both elemental sulfur and sulfate appear as the final products of chalcopyrite oxidation, which indicates that one part of the sulfide is oxidized to sulfate. However, regardless of the nature of the sulfide oxidation products, there will always be a certain number of copper and iron cations close to the chalcopyrite electrode surface which originate from the dissociation of chalcopyrite. The cations formed, as well as the corresponding oxidation number ($+1$ or $+2$ for copper, and $+2$ or $+3$ for iron), depend on the nature of the medium and the corresponding redox potential. As it is known, the hydrolyses of the cations is favored by an increase in the pH of the solution. As iron cations are hydrolyzed at lower pH values than copper ones, only the hydrolysis of iron cations will be considered in the further text.

The hydrolysis of iron cations can be described by the following equation:

$$Fe^{n+} + 2kH_2O \rightleftharpoons Fe(OH)_k^{(n-k)+} + kH_3O^+ \tag{3}$$
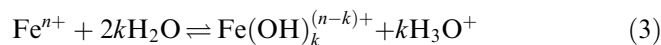
From Eq. (3) it can be seen that the formation of hydroxide will take place on the surface of the chalcopyrite electrode. Since chalcopyrite is known to be a semiconductor, the system $Fe(OH)_k^{(n-k)+} / CuFeS_2$ behaves as a hydroxysulfide/metallic electrode; its potential is defined by:

$$E = E_{ox}^{o} + \frac{RT}{nF} \ln a_{ox} a_{H_3O^+}^{k} \tag{4}$$

where $ox = Fe(OH)_k^{(n-k)+}/CuFeS_2$.

If hydrolysis leads to the formation of solid particles in the vicinity of the chalcopyrite surface, the equation for the potential of the chalcopyrite electrode can be simplified:

$$E = E_{ox}^{o} + \frac{RT}{nF} \ln a_{H_3O^+}^{k} \tag{5}$$

From Eq. (5), it follows that the potential of the chalcopyrite electrode depends on the activity of the H_3O^+ particles. Equation (5) can also be applied to non-aqueous solutions containing weak organic acids.

If the electrode reaction were reversible, as shown in the equation above, then the Nernst equation might be applicable. In a dilute aqueous solution, the activity of the water is constant, but if the Nernst equation is applied to non-aqueous solutions, the potential developed would be related to the activities of both the hydrogen ions and the water [23].

$$E = E_{ox}^{o} + \frac{RT}{nF} \ln \frac{a_{H_3O^+}^{k}}{(a_{H_2O})^{2k}} \tag{6}$$

When a methanolic KOH solution is used as the titrant in non-aqueous systems, water is produced during the neutralization of the acid sample, 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.

Potential of a chalcopyrite electrode

The Nernstain dependence of the chalcopyrite electrode was determined by following the potential of the chalcopyrite electrode with time in p-toluensulfonic acid solutions of different concentrations in the range of 0.1–0.001 M. The slope was calculated from the dependence of E versus pH obtained by plotting the electrode potential against the logarithm of the corresponding concentration. It was found that the chalcopyrite electrode shows a linear dependence with a slope of 63 mV per decade in GBL and 77 mV per decade in propylene carbonate (Fig. 2).

The response time of the chalcopyrite electrode in the investigated solvents is presented in Fig. 3, from which it can be seen that the response of the electrode remained constant with only a very slow divergence with time.

Since the chalcopyrite electrode exhibits a sub-Nernst dependence, it can not be used for the measurement of the pH of a solution, but it can be successfully applied as an indicator electrode for the titration of acids.

Titration of acids in GBL and propylene carbonate using a chalcopyrite electrode

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, such as benzoic, anthranilic, α-nitroso-β-naphthol and salicylic acid, with methanolic 0.1 M potassium hydroxide solution. The titrations of these acids (HA) in propylene carbonate [24] with KOH in methanol can be represented by the following equations:

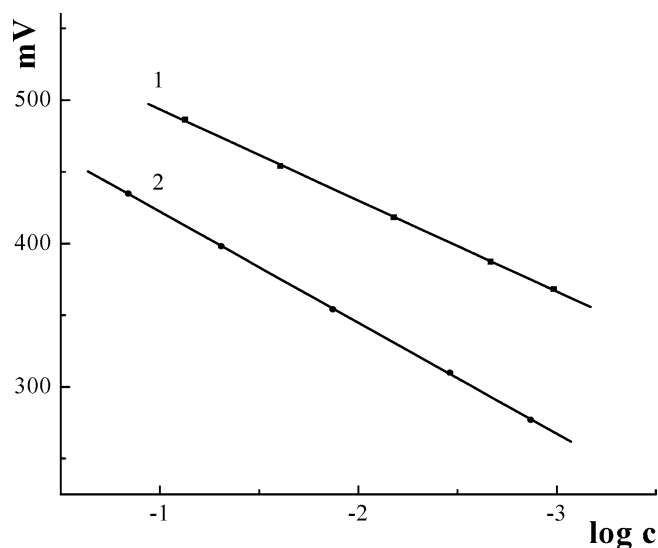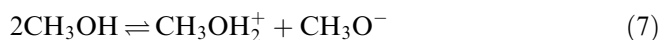In a solution of methanolic potassium hydroxide

$$2CH_3OH \rightleftharpoons CH_3OH_2^+ + CH_3O^- \tag{7}$$

Fig. 2 Plots of the chalcopyrite electrode potential versus log c (concentrations) p-toluensulfonic acid in: (1) GBL and (2) propylene carbonate
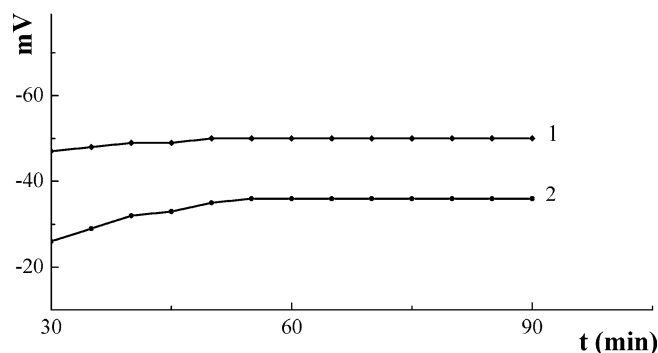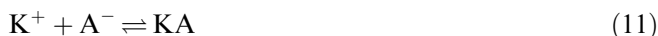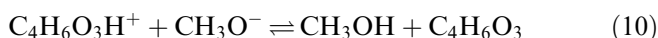

Fig. 3 Plots of the chalcopyrite electrode potential vs time in: (1) GBL and (2) propylene carbonate

$$CH_3OH_2^+ + KOH \rightleftharpoons CH_3OH + H_2O + K^+ \qquad (8)$$

In a solution of an acid

$$HA + C_4H_6O_3 \rightleftharpoons C_4H_6O_3H^+ + A^- \qquad (9)$$

During the course of a titration

$$C_4H_6O_3H^+ + CH_3O^- \rightleftharpoons CH_3OH + C_4H_6O_3 \qquad (10)$$

$$K^+ + A^- \rightleftharpoons KA \qquad (11)$$

In summary

$$HA + KOH \rightleftharpoons KA + H_2O \qquad (12)$$

The water produced in the reaction (12) has a negative effect on the titration of the examined acids with this titrant.

Previous investigations showed that methanolic potassium hydroxide is better than tetrabutylammonium hydroxide as the titrating agent in propylene carbonate [7] and hence only KOH was used in this work.

Titration curves of the acids in GBL and propylene carbonate with the electrode couples $CuFeS_2$–SCE and glass–SCE are shown in Figs. 4 and 5, respectively.

In the case of benzoic acid, the potential jumps at the equivalence point were 135 mV/0.3 ml for the chalcopyrite and 113 mV/0.3 ml for the glass electrode; see Table 1. From this table, it can also be seen that very similar jumps were obtained when the chalcopyrite or the glass electrode were used as the indicator electrode. The advantages of the chalcopyrite electrode for titrations in non-aqueous solvents can be found in the fact that a glass electrode has a limited useful life in these media because an organic solvent dehydrates its glass membrane, while the chalcopyrite electrode can be used without any measurable divergence.

When chalcopyrite was used as the indicator electrode in the applied solvents, the smallest potential jumps were obtained for α-nitroso-β-naphthol and the largest for salicylic acid.
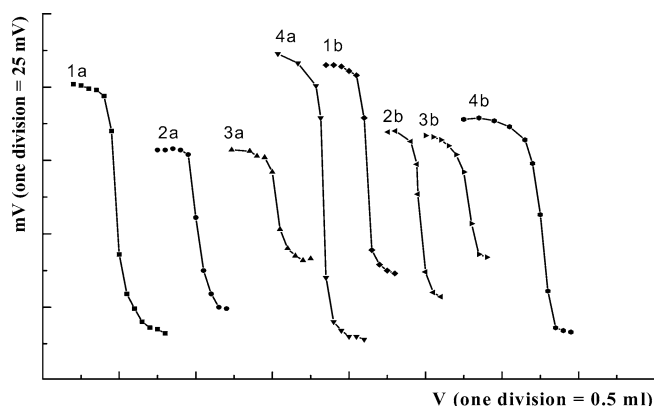

Fig. 4 The effect of the chalcopyrite (**a**) and glass (**b**) indicator electrodes on the shape of the end-point inflexion in the potentiometric titration of some acids in GBL: (1) benzoic acid; (2) antranilic acid; (3) 1-nitroso-2-naphtol; (4) salicylic acid
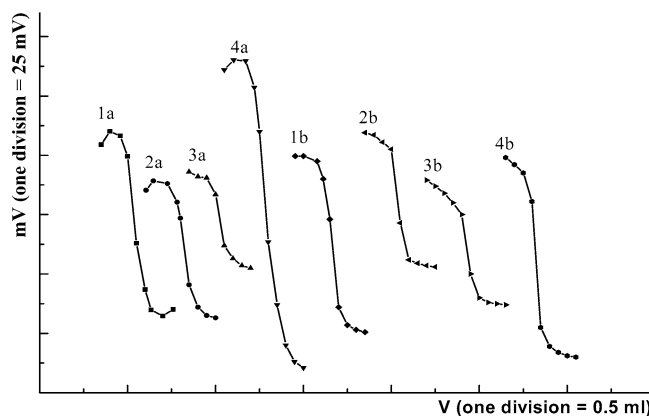

Fig. 5 The effect of the chalcopyrite (**a**) and glass (**b**) indicator electrodes on the shape of the end-point inflexion in the potentiometric titration of some acids in propylene carbonate: (1) benzoic acid; (2) antranilic acid; (3) 1-nitroso-2-naphtol; (4) salicylic acid

When the chalcopyrite electrode was employed, the potentials during the course of the titration and at the equivalence point were quickly established and the change of the potential at the equivalence point coincided with the change of the color of the applied indicator.

The results of these determinations with respect to those obtained using a glass electrode are shown in Table 2. The standard deviation for these determinations was less than 0.5 when the amount of the respective acid lay in the range 23–40 mg.

The properties of the galena mineral as conditions for the acid–base titrations in non-aqueous solutions

It is generally accepted that the oxidation of galena in aqueous media proceeds by electrochemical corrosion with oxygen reduction as the cathodic process. However, there is no agreement regarding the mechanism of the anodic process and mainly the following reaction has been suggested in the literature [25–27]:

$$PbS + 2H_2O \rightleftharpoons Pb(OH)_2 + S^o + 2H^+ + e^- \qquad (13)$$
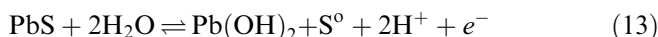
Otherwise, the electrochemical behavior of galena is similar to that of chalcopyrite. The potential of galena electrode in aqueous solution is defined by:

Table 1 Potential jumps (mV/0.3ml) at the end-point in the potentiometric titration of acids in GBL and propylene carbonate using KOH as titrant

Solvent	Titrated acid	CuFeS$_2$–SCE	PbS–SCE	Glass–SCE
γ -*Butyrolactone*	Benzoic acid	135	192	113
	Anthranylic acid	83	165	85
	α-Nitroso-β-naphthol	62	145	68
	Salicylic acid	165	230	136
Propylene carbonate	Benzoic acid	114	246	116
	Anthranylic acid	86	176	99
	α-Nitroso-β-naphthol	68	119	75
	Salicylic acid	174	281	146

Table 2 Potentiometric titration of acids in GBL and propylene carbonate using KOH as titrant

Electrode pair	Solvent	Titrated acid	Number of determinations[a]	Taken (mg)	Found (%)	Standard deviation (%)
CuFeS$_2$–SCE	γ-Butyrolactone	Benzoic acid	6	26.31	100.01	±0.44
		Anthranylic acid	6	29.94	99.63	±0.27
		α-Nitroso-β-naphthol	6	39.20	99.51	±0.48
		Salicylic acid	6	25.14	99.54	±0.32
	Propylene carbonate	Benzoic acid	6	25.60	99.94	±0.49
		Anthranylic acid	6	27.73	100.35	±0.31
		α-Nitroso-β-naphthol	6	35.59	99.98	±0.18
		Salicylic acid	6	23.68	100.11	±0.45
PbS–SCE	γ-Butyrolactone	Benzoic acid	6	26.30	99.98	±0.32
		Anthranylic acid	7	30.32	99.75	±0.21
		α-Nitroso-β-naphthol	6	39.68	99.95	±0.27
		Salicylic acid	6	25.28	99.53	±0.26
	Propylene carbonate	Benzoic acid	6	25.60	100.12	±0.31
		Anthranylic acid	6	27.73	99.86	±0.35
		α-Nitroso-β-naphthol	7	37.21	100.01	±0.30
		Salicylic acid	7	23.66	99.94	±0.26

$$E = E^o_{ox} + \frac{RT}{nF} \ln a^k_{H_3O^+} \tag{14}$$

where ox = Pb(OH$_2$)/PbS.

The potential of galena electrode in non-aqueous solution is defined by:

$$E = E^o_{ox} + \frac{RT}{nF} \ln \frac{a^k_{H_3O^+}}{(a_{H_2O})^{2k}} \tag{15}$$

Potential of a galena electrode

The values of the slope of the potential in GBL was 66 mV per decade and 98 mV per decade in propylene carbonate for concentrations of *p*-toluensulfonic acid in the range of 0.1–0.001 M (Fig. 6). The potential of a galena electrode in these solvents exhibits a sub-Nernst dependence, as does a chalcopyrite electrode.

In order to investigate the possibility of applying galena as the indicator electrode in the potentiometric titration of acids in the considered solvents, an electrode of this type was coupled with a SCE and the potential changes with the time followed (Fig. 7). From this figure, it can be seen that the potential of the galena electrode initially increased while later it remained nearly constant.

Titration of acids in GBL and propylene carbonate using of the galena electrode

Using a galena electrode, the following acids: benzoic, anthranilic, α-nitroso-β-naphthol and salicylic were titrated with a methanolic KOH solution. The titration curves of these organic acids in GBL and propylene carbonate applying the electrode couples PbS–SCE and glass–SCE are shown in Figs. 8 and 9, respectively.

The potential jumps obtained in the acid–base titrations using a galena and a glass indicator electrode are presented in Table 1. As can be seen, larger potential
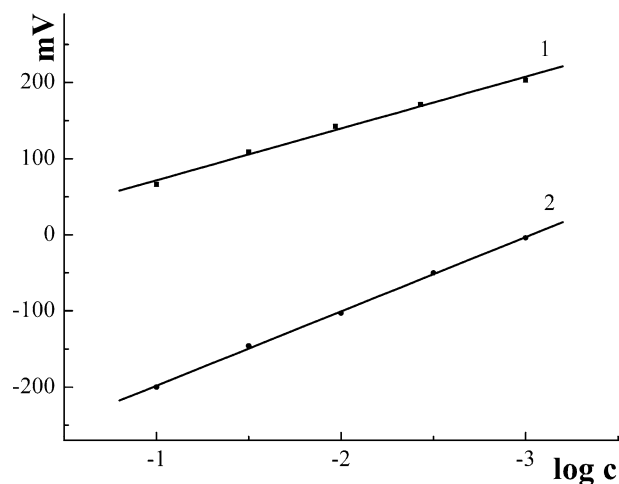

Fig. 6 Plots of the galena electrode potential vs. log *c* (concentrations) *p*-toluensulfonic acid in: (1) GBL and (2) propylene carbonate
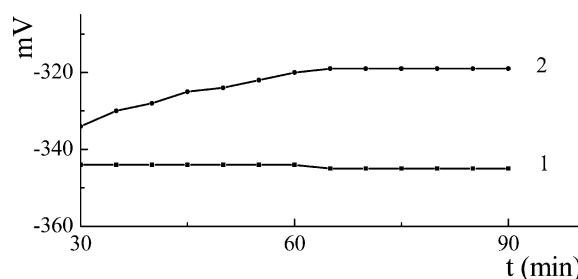

Fig. 7 Plots of the galena electrode potential vs time in: (1) GBL and (2) propylene carbonate

jumps were obtained with the galena electrode than with the glass electrode. Also, it can be seen that the potential jumps were sufficiently large (145 mV for α-nitroso-β-naphthol and 230 mV for salicylic acid in GBL, and 119 mV for α-nitroso-β-naphthol and 281 mV for salicylic acid in propylene carbonate) to allow the precise determination of these acids under the employed conditions. The standard deviations are in an acceptable
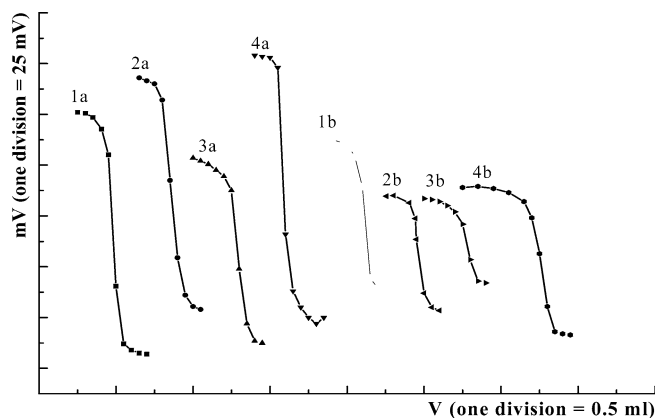
Fig. 8 The effect of the galena (**a**) and glass (**b**) indicator electrodes on the shape of the end-point inflexion in the potentiometric titration of some acids in GBL: (1) benzoic acid; (2) antranilic acid; (3) 1-nitroso-2-naphtol; (4) salicylic acid
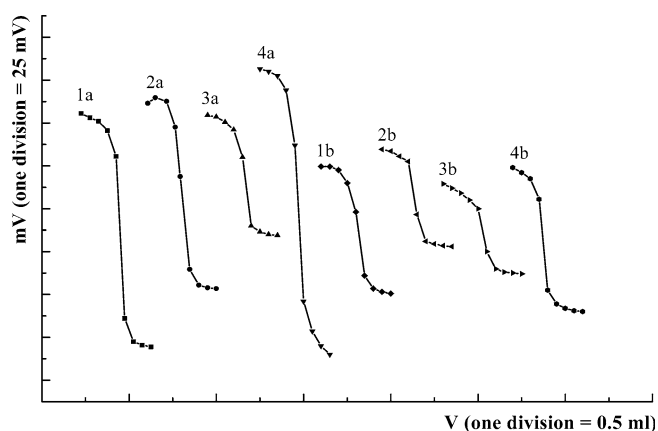

Fig. 9 The effect of the galena (**a**) and glass (**b**) indicator electrodes on the shape of the end-point inflexion in the potentiometric titration of some acids in propylene carbonate: (1) benzoic acid; (2) antranilic acid; (3) 1-nitroso-2-naphtol; (4) salicylic acid

range, indicating that this electrode can be efficiently used in acid–base potentiometric titrations (Table 2).

The addition of water to the investigated organic solvents in an amount greater than 0.5 for both investigated indicator electrodes significantly lowered the potential jump at the equivalence point, as can be seen from Table 3 and Fig. 10.

Conclusion

The obtained results show that natural monocrystalline chalcopyrite and galena can be successfully applied as indicator electrodes for the titration of weak acids in GBL and propylene carbonate. The rapid establishment of the equilibrium potentials in the course of the titration, the sufficiently high potential jumps at the equivalence point and their chemical inertness in the working media make these electrodes very suitable for such determinations. Further investigations have shown that

Table 3 Potential jumps (mV/0.3 ml) at the end-point in the potentiometric titration of benzoic acid in GBL and propylene carbonate at different concentrations of water

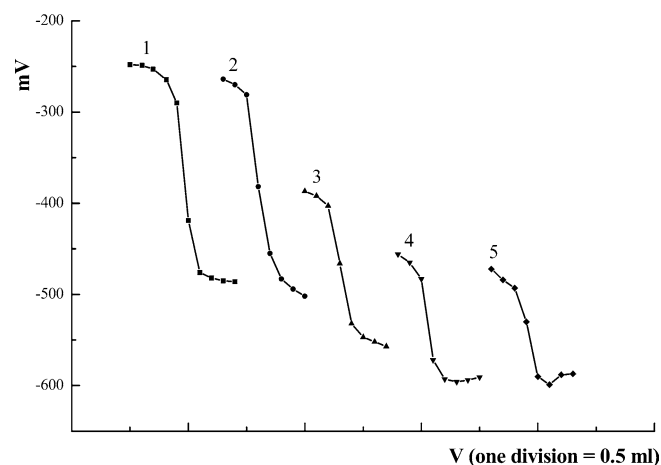| Solvent	Water (%)	CuFeS$_2$–SCE	PbS–SCE
γ -*Butyrolactone*	Non-aqueous media	135	192
	0.5	105	185
	1.0	89	144
	5.0	61	128
	10.0	53	106
Propylene carbonate	Non-aqueous media	114	246
	0.5	108	204
	1.0	85	167
	5.0	64	106
	10.0	55	92

Fig. 10 Potentiometric titration curves of benzoic acid in GBL obtained by using a galena indicator electrode: (1) non-aqueous solution; (2) 0.5%, (3) 1.0%, (4) 5.0% and (5) 10.0% water in GBL

the chalcopyrite and galena electrodes can be successfully used in precipitation, complexometric and redox titrations in water as well as acid–base titrations in other non-aqueous solvents.

Moreover, the simple construction, inexpensive production and high accuracy of these electrodes show their potential for application in the pharmaceutical industry. Studies aimed at investigating this hypothesis are in progress.

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