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Natural metal sulfides as electrochemical sensors for redox titrations in γ-butyrolactone and propylene carbonate

Zorka Stanić · Jelena Stepanović

Abstract Natural monocrystalline pyrite, chalcopyrite, and galena have been used as indicator electrodes for potentiometric redox titrations in γ-butyrolactone and propylene carbonate. Copper(II) solution was employed as the titrating agent. The results obtained by using these electrodes were compared with those obtained by application of a platinum electrode under the same conditions, and good agreement, reproducibility, and accuracy were obtained. The results deviated by 0.16–0.50% from those obtained by using a platinum electrode. All the electrodes showed a relatively fast response time and can be used without any time limit or without considerable divergence in the potentials. The potential jumps at the titration endpoint obtained in the titration of some compounds by using a pyrite electrode are higher than those obtained by application of platinum as the indicator electrode.

Keywords Pyrite · Chalcopyrite · Galena · Redox titration · γ-Butyrolactone · Propylene carbonate

Introduction

Potentiometric ion-selective electrodes (ISEs) are among the most important groups of chemical sensors. The application of ISEs has evolved to a well-established routine analytical technique in many fields, including clinical and environmental analysis, physiology, and process control. The essential part of an ISE is the ion-selective membrane. The membrane may be a glass, a crystalline solid, or a liquid. A glass membrane is still superior to other sensor types in a variety of applications, including biomedical, industrial, and environmental. The glass pH electrode is the most widespread sensor, being present in the arsenal of virtually any laboratory. Although the performance of the best glass membrane sensors remains unsurpassed, the chemical versatility of these materials is limited, which imposes restrictions on the range of available analytes. During recent decades research and development of potentiometric sensors has shifted primarily towards the more versatile and tunable solid-state membrane ISEs.

Many publications report solid-state membrane compositions with selective response to particular ionic species [1–3]. More recently solid membrane electrodes have been prepared using polymer matrix materials [4]. Deshmukh and Coetzee [5, 6] detail their work on the use of various membrane electrodes and potentiometric titration to detect contaminants in nonaqueous solvents. Other researchers have reported on the response of copper(II) and cadmium membrane electrodes in some nonaqueous solvents [7]. For potentiometric determinations in non-aqueous solutions the natural metal sulfides have been extensively used [8, 9].

During the past several decades various ion-selective electrodes have been tested in non-aqueous dipolar aprotic solvents, for example 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 [10]. Acid–base equilibria of some acids have been examined in propylene carbonate using glass and Ag/AgClO₄ electrodes [11]. Coetzee and Martin [12] evaluated the response of a single-crystal lanthanum fluoride electrode in both direct potentiometry and potentiometric titrations in PC

Z. Stanić (✉) · J. Stepanović
Department of Chemistry, Faculty of Sciences,
University of Kragujevac,
P.O. Box 60, R. Domanović 12,
34000 Kragujevac, Serbia
e-mail: zorkas@kg.ac.rs

and in its mixture with water. Potentiometric acid–base determinations have been carried out in this solvent with antimony, anodically polarized platinum, and preheated platinum electrodes [13]. Coetzee et al. [14] reported the potentiometric characterization of γ-butyrolactone using ion-selective electrodes. The dissociation constants of some acids and protonated bases in GBL have been determined and the pK_A values obtained have been compared with those in PC [15]. The results obtained with an iridium oxide pH-sensor in GBL and PC solvents were compared with those obtained with a glass electrode and pH-ISFETs [16].

Proceeding from the fact that γ-butyrolactone and propylene carbonate are good solvents for electrochemical redox investigations with wide potential windows on the two sides [10], and that the minerals pyrite, chalcopyrite, and galena have been used as sensors for detecting the titration end point (TEP) in acid–base titrations in some non-aqueous solutions [8, 9], the purpose of this study was to investigate the behavior of these electrodes as electrochemical sensors in the redox determination of some organic compounds using γ-butyrolactone and propylene carbonate as the solvents. The electrochemical investigations were carried out by performing potentiometry experiments.

Results and discussion

General considerations

Currently, solid-state membrane electrodes without an internal solution play an important role in chemical studies in non-aqueous solutions. Previous investigations have shown that the mineral pyrite (FeS_2) can be applied as a sensor for the detection of the TEP in aqueous [17] and non-aqueous media [9]. It was also found that monocrystalline chalcopyrite ($CuFeS_2$) and galena (PbS) can be successfully applied in non-aqueous solutions [8]. Taking into account that copper is already involved in the structure of pyrite (chalcopyrite), and that chemical analysis of galena indicated the presence of copper in this mineral, it was of interest to investigate the behavior of these electrodes as electrochemical sensors for potentiometric redox titrations in γ-butyrolactone and propylene carbonate, using copper(II) solution as the titrating agent.

Stability and response time are important factors for an electrode. In this study, in order to investigate the practical applicability of pyrite, chalcopyrite, and galena as indicator electrodes in the potentiometric redox titration of different compounds in the solvents considered, the electrodes were coupled with a modified saturated calomel electrode (SCE) and the potential changes with the time were followed. In

both of the investigated solutions stable potentials were attained for approximately 5 min.

The response time of the pyrite electrode was determined by recording the time elapsed before a stable potential value was attained after the pyrite electrode and the reference electrode (modified SCE) were immersed in calibration solutions from low to high concentrations of Cu(II) solutions (0.001–0.1 mol dm^{-3}). The change of the electrode potential for the pyrite electrode ranged from +461 to +859 mV in propylene carbonate and from +369 to +709 mV in γ-butyrolactone as solvents. The response time for the pyrite electrode was 10 s in propylene carbonate and 12 s in γ-butyrolactone. In addition, chalcopyrite and galena electrodes showed a relatively fast response time in the investigated solvents (less than 15 s).

The electrodes worked well without any time limit and without observing any significant change in the practical response time.

Analytical utilization of the electrodes

The practical utility of the sensors was tested by their use as indicator electrodes for redox titration of ferrocene, tetrabutylammonium iodide, thiourea, and phenylhydrazine with 0.04 mol dm^{-3} copper(II) solution in γ-butyrolactone and propylene carbonate.

Ferrocene oxidation by copper(II)

Four possible electrode couples for detection of the end point in the potentiometric titrations of ferrocene with copper(II) solution were considered: namely, FeS_2–SCE, $CuFeS_2$–SCE, PbS–SCE, and Pt–SCE (Fig. 1). Ferrocene is oxidized rapidly and stoichiometrically to the ferricinium ion by copper(II) in γ-butyrolactone and propylene carbonate:

$$Fc + Cu(II) \rightleftharpoons Fc^+ + Cu(I) \qquad (1)$$
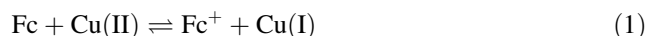
When the process was followed using FeS_2, $CuFeS_2$, and Pt electrodes, large breaks in potential were found in the vicinity of the equivalence point. In addition, ferrocene was found to have very good stability in the solutions.

Thiourea oxidation by copper(II)

Figure 2 shows titration curves for the oxidation of thiourea with copper(II) solution as the titrating agent in γ-butyrolactone and propylene carbonate. The copper(II)–thiourea reaction stoichiometry is 1:1, therefore, formation of the disulfide is postulated. Because the thiourea–copper(II) reaction proceeds rapidly even under anhydrous conditions, the disulfide product must act as a base to give a species of the form $[(H_2N)_2CS]_2^{+2}$.
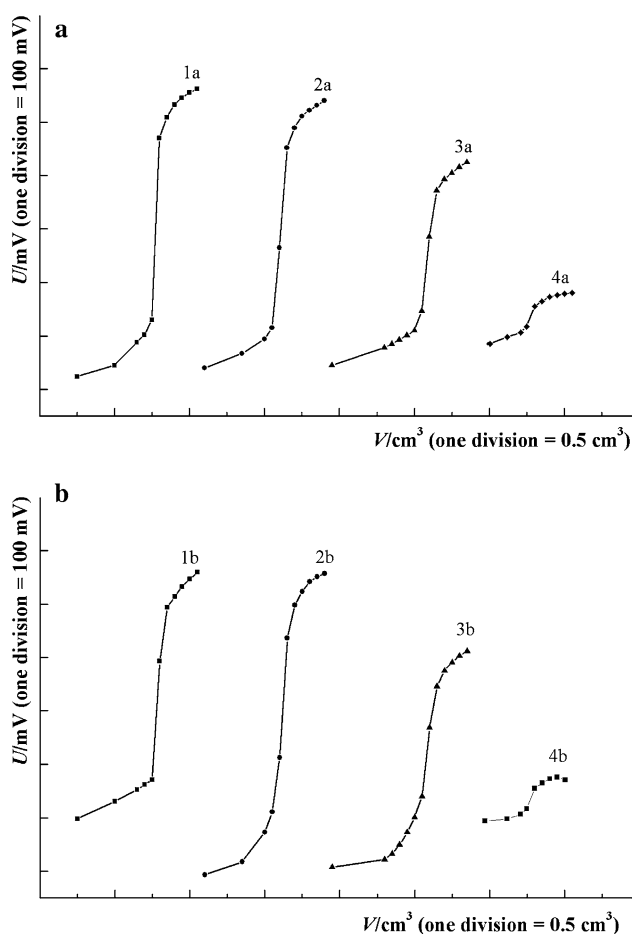
Fig. 1 The effect of the platinum (*1*), pyrite (*2*), chalcopyrite (*3*), and galena (*4*) indicator electrodes on the shape of the end-point inflection in the potentiometric titration of ferrocene in propylene carbonate (**a**) and γ-butyrolactone (**b**) using copper(II) as titrant
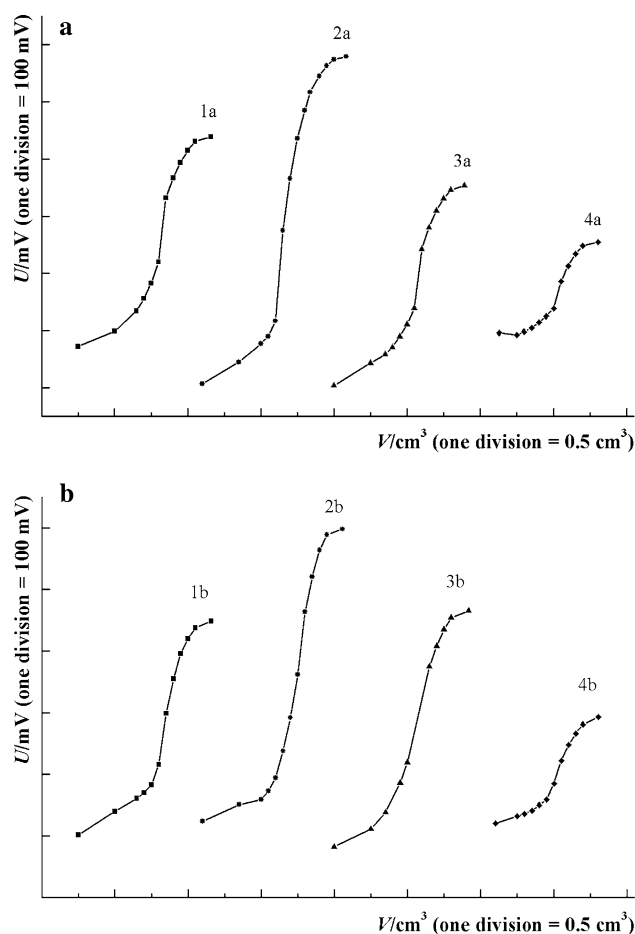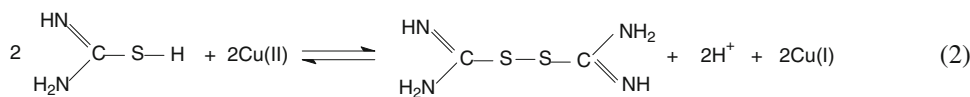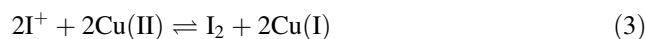

Fig. 2 The effect of the platinum (*1*), pyrite (*2*), chalcopyrite (*3*), and galena (*4*) indicator electrodes on the shape of the end-point inflection in the potentiometric titration of thiourea in propylene carbonate (**a**) and γ-butyrolactone (**b**) using copper(II) as titrant

$$2 \, \text{(thiourea)} \, + 2\text{Cu(II)} \rightleftharpoons \text{(dithiourea)} \, + \, 2\text{H}^+ \, + \, 2\text{Cu(I)} \qquad (2)$$

Tetrabutylammonium iodide oxidation by copper(II)

When tetrabutylammonium iodide is titrated with copper(II) solution, it is oxidized in two steps (Fig. 3). The first inflection point corresponds to the formation of the triiodide ion, and the second to the oxidation of the triiodide ions to iodide: $I^- \rightarrow I_3^-$ and $I_3^- \rightarrow I_2$. This assignment was confirmed by the conversion of a weighed sample of iodide to triiodide by addition of excess iodine, followed by titration. Only one inflection point, corresponding to the potential of the second potential jump seen previously, was observed at a 1:1 copper(II)–iodide ratio.

The stoichiometry of the reaction of tetrabutylammonium iodide with copper(II) can be formulated in the following way:

$$2I^+ + 2\text{Cu(II)} \rightleftharpoons I_2 + 2\text{Cu(I)} \qquad (3)$$

Phenylhydrazine oxidation by copper(II)

A gradual increase in potential is observed with progressive addition of the oxidant to the solution of phenylhydrazine. A sharp jump in potential is registered at the end point of the titration (Fig. 4). The stoichiometry of the reaction can be formulated in the following way:
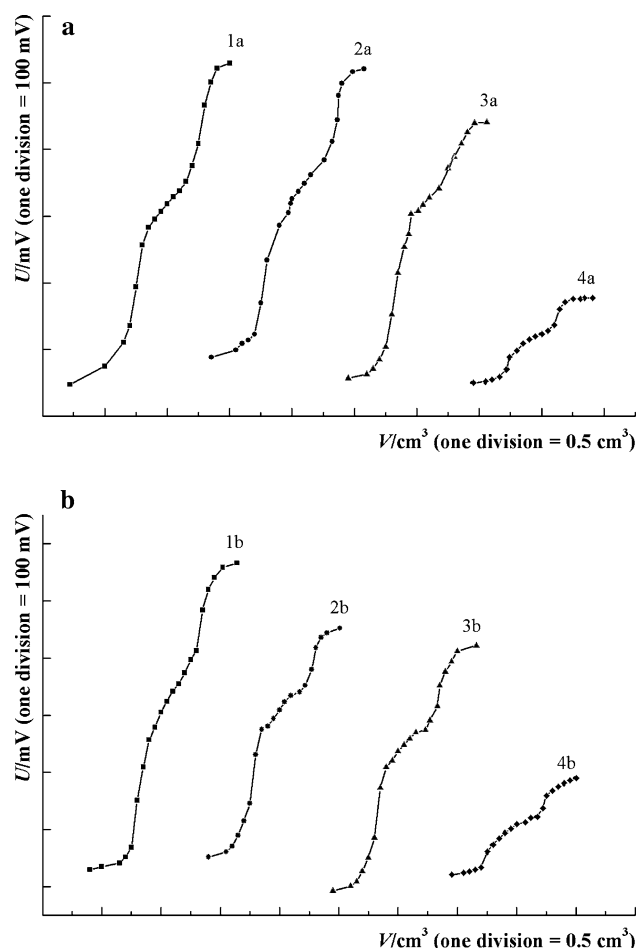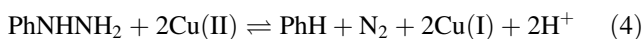
Fig. 3 The effect of the platinum (*1*), pyrite (*2*), chalcopyrite (*3*), and galena (*4*) indicator electrodes on the shape of the end-point inflection in the potentiometric titration of tetrabutylammonium iodide in propylene carbonate (**a**) and γ-butyrolactone (**b**) using copper(II) as titrant

$$PhNHNH_2 + 2Cu(II) \rightleftharpoons PhH + N_2 + 2Cu(I) + 2H^+ \quad (4)$$

It can be seen that two moles of the oxidant are required for every mol of phenylhydrazine. Phenylhydrazine is oxidized rapidly and quantitatively.

The potential jumps at the equivalence point

The potential jumps obtained in the redox titrations in γ-butyrolactone and propylene carbonate by applying the electrode couples FeS$_2$–SCE, CuFeS$_2$–SCE, PbS–SCE, and Pt–SCE are presented in Table 1. From the table it can be seen that very similar jumps were obtained when the pyrite or the platinum electrode were used as the indicator electrodes. Moreover, larger potential jumps were obtained with the pyrite electrode than with the platinum electrode for most of the compounds used in γ-butyrolactone as a solvent.
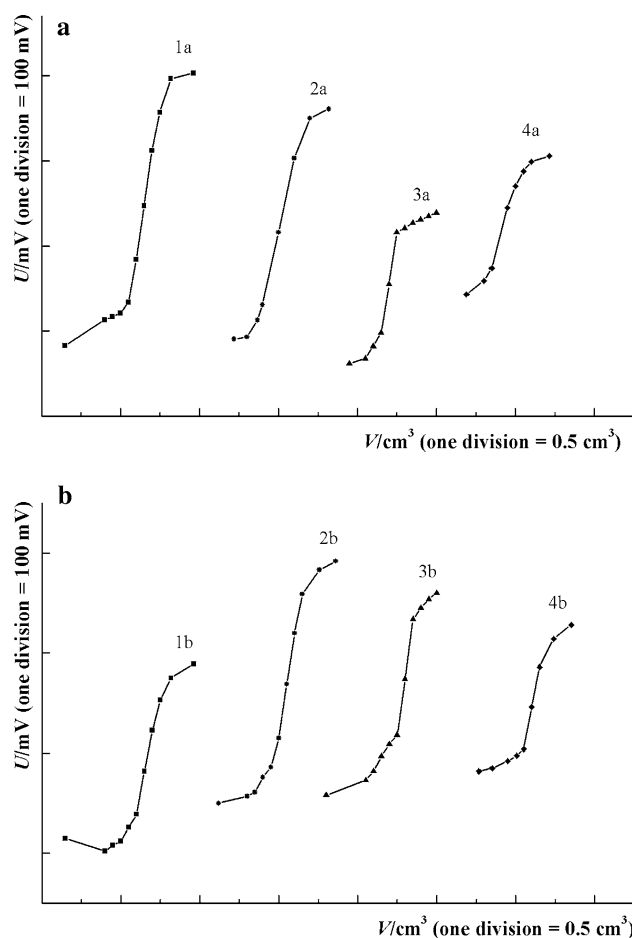

Fig. 4 The effect of the platinum (*1*), pyrite (*2*), chalcopyrite (*3*), and galena (*4*) indicator electrodes on the shape of the end-point inflection in the potentiometric titration of phenylhydrazine in propylene carbonate (**a**) and γ-butyrolactone (**b**) using copper(II) as titrant

In the case of phenylhydrazine, the jumps at the equivalence point in γ-butyrolactone were 134 mV/0.3 cm^3, 127 mV/0.3 cm^3, 85 mV/0.3 cm^3, and 97 mV/0.3 cm^3 for the pyrite, chalcopyrite, galena, and platinum electrodes, respectively. For the same compound in propylene carbonate as a solvent the jumps at the equivalence point were 142 mV/0.3 cm^3, 123 mV/0.3 cm^3, 86 mV/0.3 cm^3, and 173 mV/0.3 cm^3 for the pyrite, chalcopyrite, galena, and platinum electrodes, respectively. When galena was used as the indicator electrode, in both of the applied solvents the largest potential jumps were obtained for phenylhydrazine. In addition, it can be seen that the potential jumps for ferrocene were sufficiently large when applying the indicator electrodes FeS$_2$ (387 and 374 mV in γ-butyrolactone and propylene carbonate, respectively) and CuFeS$_2$ (245 and 262 mV in γ-butyrolactone and propylene carbonate, respectively) to enable precise determination of this compound under the employed conditions.

Table 1 Potential jumps (mV/0.3 cm^3) at the end-point in the potentiometric titration of different type of compounds in γ-butyrolactone and propylene carbonate using copper(II) as titrant

Solvent	Titrated compound	FeS$_2$–SCE	CuFeS$_2$–SCE	PbS–SCE	Pt–SCE
γ-Butyrolactone	Ferrocene	387	245	28	332
	Tetrabutylammonium iodide	79	77	40	123
	Thiourea	229	156	77	172
	Phenylhydrazine	134	127	85	97
Propylene carbonate	Ferrocene	374	262	33	407
	Tetrabutylammonium iodide	93	79	27	125
	Thiourea	249	170	88	184
	Phenylhydrazine	142	123	86	173

As regards lifetime and sensitivity, the natural monocrystalline sensors gave good results in non-aqueous solvents a year after their preparation—results were similar to those obtained with the freshly prepared electrodes. The results obtained in this work confirm that there is no statistically significant difference between theoretical and found values. The relative standard deviations in the determination of all of the compounds were in a range 0.16 to 0.50% when the amount of the respective compound lay in the range 5–47 mg.

Conclusions

The objective of sensor research for many years was to produce rugged, solid-state devices with rapid, sensitive response and exquisite selectivity, that could be mass-produced at low cost. Furthermore, the array of sensors must be exposed in a very reproducible manner to the sample, and after measurements the array must be conditioned in a reproducible way before the next analyte is introduced.

In this paper, the use of natural monocrystalline pyrite, chalcopyrite, and galena as electrochemical sensors for potentiometric redox titrations in γ-butyrolactone and propylene carbonate is reported for the first time. The main observations and conclusions have been summarized as follows:

1. The results obtained in this work confirm that natural monocrystalline pyrite, chalcopyrite, and galena can be successfully applied as indicator electrodes for redox titrations in γ-butyrolactone and propylene carbonate.
2. The equilibrium potential in the course of the titration and at the titration end-point is rapidly established.
3. Copper(II) solution proved to be a very suitable titrating agent for these redox titration in γ-butyrolactone and propylene carbonate.
4. Taking into account the simple construction, chemical inertness in the working media, inexpensive production,

and high accuracy of these electrodes, it may be concluded that pyrite, chalcopyrite, and galena as sensors of indicator electrodes can be efficiently used in potentiometric redox titrations.

More detailed and systematic studies on the use of the pyrite, chalcopyrite, and galena electrodes in non-aqueous solutions are now in progress; these include some practical applications in the pharmaceutical industry.

Experimental

Reagents

All chemicals used in this study were of analytical reagent grade from either Merck or Fluka. γ-Butyrolactone and propylene carbonate (Fluka) were puriss. p.a. purity ($\geq$99%). These solvents were used without further purification. Prior to use acetonitrile was purified by a procedure described in the literature [18].

Commercial ferrocene was purified by recrystallization from heptane; the product was dried under vacuum for at least 12 h. Tetrabutylammonium iodide was analyzed as received for iodide by precipitation as AgI. Thiourea was recrystallized from ethanol. Phenylhydrazine was used as supplied by Merck.

Hydrated copper(II) perchlorate, $Cu(ClO_4)_2 \cdot 6H_2O$, was prepared by adding a slight excess of 72% perchloric acid to a suspension of copper(II) carbonate in water. The solution was boiled to eliminate carbon dioxide, then cooled, and the resulting crystals were collected and dried at room temperature under vacuum.

Freshly hydrated copper(II) perchlorate solution, approximately 0.04 mol dm^{-3}, was prepared in pure acetonitrile, and copper(II) was determined by EDTA titration in aqueous solution using murexide, mixed 1:1,000 by weight with sodium chloride, as the indicator [19]. The solution was stored in a borosilicate glass bottle with a ground-glass stopper.

The solutions of the investigated compounds (0.04 mol dm^{-3}) were prepared by weighing an appropriate amount of the compound and dissolving in the desired volume of the corresponding solvent.

Apparatus and electrodes

The potential changes of the pyrite, chalcopyrite, and galena electrodes with time and the oxidation reactions were followed with a Digital 870 pH-meter (Dresden) using pyrite, chalcopyrite, galena, and platinum as the indicator electrodes and SCE as the reference electrode.

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

The indicator galena electrode was prepared in the following manner: A quadratic piece of galena ($a = 0.5$ cm) was used as the electrode material. The galena electrode was made by polishing the galena crystal with diamond paste, and it 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 copper wire was immersed in the mercury and this device was mounted in a wider glass tube ($\phi = 1$ cm), which was then cemented with a cold sealing mass based on methyl methacrylate. After solidification of this mass, the working surface of the electrode was polished to a high gloss. The electrode was then rinsed with distilled water and alcohol and dried in air, after which it was ready for use. The pyrite and chalcopyrite indicator electrodes were prepared in a similar manner.

The response of the indicator pyrite, chalcopyrite, and galena electrodes in γ-butyrolactone and propylene carbonate was compared with that of a conventional platinum electrode.

The reference electrode was a modified saturated calomel electrode. Modification of the normal SCE of the type 401 (Radiometer, Copenhagen) was achieved by complete replacement of its inner solution with a saturated solution of potassium chloride in anhydrous methanol. The electrode was modified to reduce the liquid junction potential between the inner solution of the SCE and investigated solution.

Procedures

Potential measurement
The change of the potential of the pyrite, chalcopyrite, and galena electrodes with time was followed in GBL and PC as solvents. These indicator electrodes were coupled with a modified saturated calomel electrode as the reference electrode.

Potentiometric titration
A known volume (10 cm^3) of the solvent was placed in the titration vessel and a measured volume of the substance to be investigated (ca. 0.13 mmol) was added. The indicator electrode, either pyrite, chalcopyrite, or galena, or a platinum electrode, and a modified SCE as the reference electrode were immersed in the solution and connected to a pH-meter. Potentiometric titration was then carried out by addition of 0.05 cm^3 aliquots of a standard copper(II) solution of 0.04 mol dm^{-3}. The solution was vigorously stirred with a magnetic stirrer during the titration. 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 end-points were determined classically from the second derivative of the titration curve. All experiments were carried out under an argon atmosphere at room temperature.

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