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Natural monocrystalline pyrite as a sensor in non-aqueous solution Part I: Potentiometric titration of weak acids in, *N*,*N*-dimethylformamide, methylpyrrolidone and pyridine

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Abstract

The possibility of applying natural monocrystaline pyrite as a sensor for the potentiometric titration of weak acids in *N*,*N*-dimethylformamide, methylpyrrolidone and pyridine was investigated. The potential of this electrode in *N*,*N*-dimethylformamide, methylpyrrolidone and pyridine exhibits a sub-Nernst dependence. In *N*,*N*-dimethylformamide the slope (mV/pH) is 39.0 and in methylpyrrolidone it is 45.0. The potential jumps at the titration end-point obtained in the titration of weak acids are higher than those obtained by the application of a glass electrode as the indicator electrode The potential in the course of the titration and at the titration end-point (TEP) are rapidly established. Sodium methylate, potassium hydroxide and tetrabutylammonium hydroxide (TBAH) proved to be very suitable titrating agents for these titrations. The results obtained in the determination of the investigated weak acids deviate by 0.1–0.35% with respect to those obtained by using a glass electrode as the indicator electrode.

Keywords: Potentiometry; Natural monocrystalline pyrite; Sensor; Non-aqueous media

1. Introduction

Very weak acids and weak acids are commonly titrated in basic solvents such as *N*,*N*,-dimethylformamide, methylpyrrolidone and pyridine.

A glass electrode is widely used as the indicator electrode in non-aqueous as well as in aqueous titrations. Its response to ($pH = -\log a(H^+)$) has been shown to be Nernstian in various non-aqueous solvent [1] and many acid dissociation constants in aprotic solvent have been obtained by using a glass electrode as pH-sensor [2]. However, in non-aqueous media, these electrodes show certain undesirable features: the potential response of a glass electrode in non-aqueous solutions is often very slow. In some cases, it takes over 1 h before the equilibrium potential is reached. Efforts have been made to improve the response speed of a glass electrode, but without sufficient success [3]. Apart from this, they tend to behave erratically and their behavior depends on the nature and extent of pretreatment or "condition" of the electrode. In addition, the electrodes have a limited useful life when employed in non-aqueous titration because the solvents dehydrate the glass membrane, thereby reducing its affinity for, or response to, hydrogen ions. In the basic range in non-aqueous solution, a glass electrode exhibits an alkaline error [4], so that the e.m.f. jump may be diminished or even fail to appear during a titration [5]. Allen and Geddes [6] found that a glass electrode did not respond to all to changes of acidity of an ethylenediamine solution containing sodium ions. Harlow [7] obtained complex titration curves in pyridine when the titrant contained potassium ions. While titrating picric acid with quaternary tetrabutylammonium hydroxide (TBAH) using a glass electrode as the indicator, Izutsu et al. [8] obtained distorted curves when GBL was used as the solvent as the result of the hydrolysis of GBL with acids-bases. Thus, it is difficult to obtain reliable information with a glass electrode. The glass electrode re-

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sponse was shown to be slow in 2-propanol when the solution was changed from basic to acidic [9]. The e.m.f. change was correlated with ion-exchange processes in the gel-layer. In the basic region, hydrogen ions in the gel-layer were replaced by alkali metal ions. The reverse exchange occurred on making a basic solution containing alkali metal ion more acidic, as would happen during the titration of a base with an acid. Despite the small total amount of exchanged ions, about 10^{-8} moles cm^{-2} of glass area for most hydrogen ion glass electrode, the exchange process is slow and results in an e.m.f. which varies with time.

As alternatives to a glass electrode, metal and metalloid indicator electrodes, metallic electrodes coated with a layer of hydroxide or oxide, metal hydrides and some minerals can be used [10–38].

Mihajlović et al. [39] used Pt-$(H_2/Pd)_{ref}$ and Sb-$(H_2/Pd)_{ref}$ electrode systems in PC (propylene carbonate) for the coulometric–potentiometric titration of organic bases and in the potentiometric titration of mineral and organic acids, as well as of di-component acid mixtures. The platinum electrode was pre-treated with hydrogen peroxide, iron(II)-sulphate or nitric acid, or it was anodically or cathodically polarized or heated to glowing.

Mihajlović et al. [40–50] applied H_2/Pd and D_2/Pd electrodes as the indicator and reference electrode for the titration of acids and bases in water and non-aqueous media.

Antonijević, et al. [51] have used natural monocrystalline pyrite as the electrode material for the potentoiometric titration of acids in water.

In this work the possibility of applying a pyrite sensor for the potentiometric determination of weak organic acids in *N*,*N*-dimethylformamide, methylpyrrolidone and pyridine as solvents has been investigated.

2. Experimental

2.1. Reagents

All the used chemicals were of analytical reagent grade (Merck and Fluka). *N*,*N*-Dimethylformamide, *N*-methylpyrrolidone and pyridine (Fluka) were puriss p.a. purity: pyridine (≥99.8%) with water content ≥0.05%, *N*,*N*-dimethylformamide (≥99.8%) with water content (≥0.05%) and methylpyrolidone (≥99%) with water content ≥0.1%. These solvents were used without further purification. We checked the water content in the applied solvents by using Karl Fischer titration.

Solution of acids were used as primary standards or their concentrations were previously determined by titrating them with standard Bu_4NOH (tetra-*n*-butylammonium hydroxide) by using visual or potentiometric, applying glass electrode-modified SCE electrode couple, end-point detection; a 0.1 mol L^{-1} solution was used. The solvent contained about 0.1% of water. Methanolic potassium hydroxide was prepared according to Kreshkov, et al. [52].

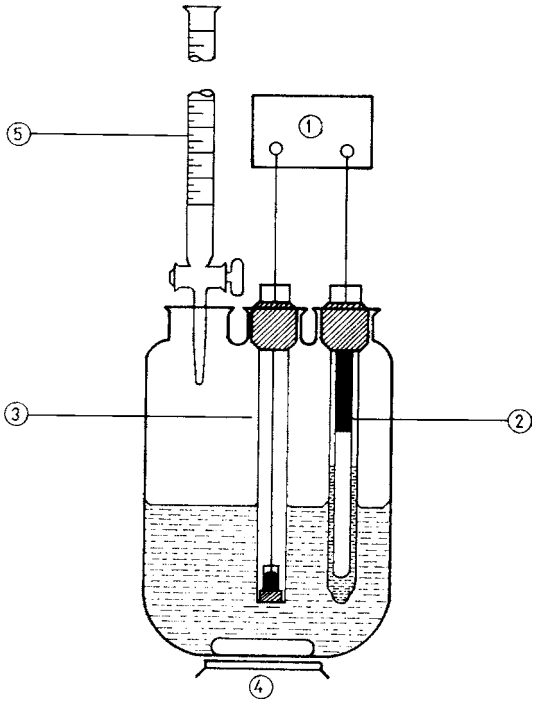

Fig. 1. Scheme of the apparatus for potentiometric titration of acids: (1) pH-meter; (2) indicator electrode (pyrite electrode or glass electrode); (3) reference electrode (SCE or H_2/Pd); (4) magnetic stirrer.

Tetra-*n*-butyl ammonium hydroxide (laboratory-reagent grade) 0.1 M solution in toluene–methanol (3:1 v/v) was standardized against an aqueous solution of potassium hydrogen phthalate with phenolphthalein as indicator. A solution of sodium methylate in a mixture of benzene and methanol was prepared according to Kreshkov, et al. [52]. A 0.1% solution of Thymol Blue was used as the indicator.

The stationary potential of the pyrite electrode was measured in a freshly prepared solution of *p*-toluene-sulfonic acid within the concentration range of 5.10^{-2} to 5.10^{-3} M in *N*,*N*-dimethylformamide and 5.10^{-2} to $2.5.10^{-4}$ M in

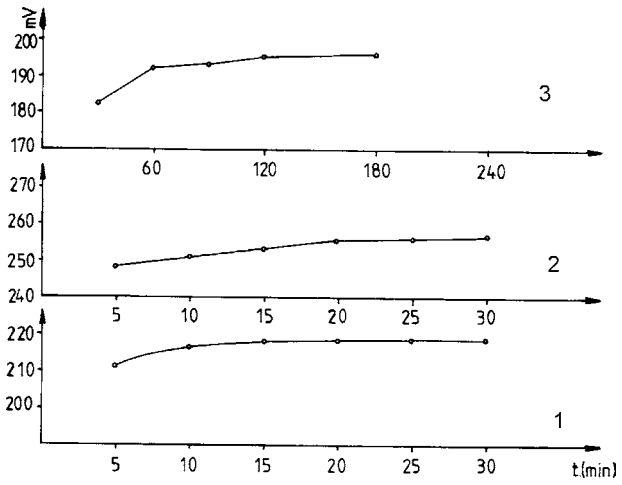

Fig. 2. Plots of the pyrite electrode potential versus time *p*-toluene-sulfonic acid in: 1. *N*,*N*-dimethylformamide; 2. methylpyrrolidone; 3. pyridine.

N-methylpyrrolidone (Figs. 3 and 4, respectively). In all the investigated solutions, a stable potential was attained in less than 5–6 min. The results (Fig. 2) represent the data obtained by measuring the potential of the pyrite electrode after standing for 30 min in the respective solution.

The volume of acid was measured by means of a micro burette with a PTFE tip; for visual end-point detection, 1.00 mL of the investigated acid was taken, whereas for potentiometer end-point detection, 2.00–3.00 mL of acid were used.

2.2. Electrodes

The pyrite electrode has been described in our earlier paper [51]. The H_2/Pd reference electrode was made of palladium saturated with hydrogen, and immersed in 0.2 M sodium perchlorate or tetra-*n*-butyl ammonium hydroxide in the appropriate solvent, placed in a glass tube with a sintered-glass (G-4) bottom.

A glass electrode type G-202C (Radiometer, Copenhagen) and a calomel electrode type 401 (Radiometer, Copenhagen) with potassium chloride in methanol were used as the reference electrode. The glass electrode was conditioned in the appropriate solvent before use.

The indicator pyrite electrode was coupled either with a saturated calomel electrode or with an H_2/Pd-electrode as the reference electrode and the change of the potential with time was followed. The changes of the potential of the pyrite electrode with time in a solution of the appropriate acid in the corresponding solvents are shown in Fig. 2.

2.3. Apparatus

The apparatus used for following the potential changes as a function of c (sulfanilic acid) and for end-point detection with pyrite electrode–SCE, pyrite electrode–H_2/Pd reference electrode and glass electrode–SCE couples is shown in Fig. 1. The potentials during course of the titration were measured using a pH-meter type pHM-62, Radiometer, Copenhagen, or a Digital 870 pH meter.

2.4. Procedure

Certain volume (12 mL) of solvent is measured, three drops of indicator are added and the solvent is titrated with appropriate titration substance until the change of colour of the indicator. Then, certain volume of investigated acid is measured and appropriate electrode pair (pyrite electrode–SCE, pyrite electrode–H_2/Pd or glass electrode–SCE) is immersed in the solution. The solution was then titrated potentiometrically by adding 0.05 or 0.1 mL increments of 0.1 M tetra-*n*-butylammonium hydroxide (potassium hydroxide or sodium methoxide) and measuring the potential immediately before the addition of each increment. The potential measurements were made at 2 min intervals at the beginning of the titration and at 4 min intervals in the region within ±0.3 mL of the end-point. Increments of 0.1 mL were the minimum that could reasonably be reproduced with the burette used. The titration end-point was determined the second derivative method.

3. Results and discussion

Various inorganic bases, acetates of alkaline metals, alkolates of alkali metals and many different organic bases have been used as base titrants for the titration of compounds with acid properties in non-aqueous solvents. Sodium and potassium hydroxide in methanol [53], ethanol [54,55], 2-propanol [56,57], acetates of alkali metals [58] and methylates, ethylates and 2-propylates of sodium, potassium and lithium [59–61] were frequently applied.

Amines, such as diphenyl guanidine, pyridine, morpholine, tetramethyl, tetraethyl and tetrabutyl ammonium hydroxide, are the most frequently used base titrants [62,63]. In all our investigations of the behavior of a pyrite electrode as an indicator electrode in pyrrolidone, dimethylformamide and pyridine, sodium methylate, KOH in anhydrous methanol and TBAH in a mixture of 2-propanol/methanol were used as titrants.

3.1. Mechanism

Pyrite is only slightly soluble in water, like all other similar sulphides. The dissociation of pyrite gives rise to Fe(II) cations and sulphur anions. Fe(II) ions can be oxidized to Fe(III) ions by oxygen dissolved in water. Fe(III) ions can also be formed in the solution by the oxidation of pyrite when oxygen is present in the solution, since pyrite is a good catalyst for the reduction of oxygen. The cathodic reduction of oxygen causes the anodic dissolution of pyrite according to the equation:

$$FeS_2 + 8H_2O = Fe^{2+} + 2\,SO_4{}^{2-} + 16\,H^+ + 14e \quad (1)$$

In a solution into which a pyrite electrode is immersed, the aforecited properties of pyrite bring about the formation of Fe(II) and Fe(III) ions. It is known that with increasing pH values of the solution, these ions undergo hydrolysis which can be represented by the following equation:

$$Fe^{n+} + 2\,kH_2O = Fe(OH)_k{}^{(n-k)+} + kH_3O^+ \quad (2)$$

Reaction (2) shows the formation of hydroxide in a layer near the pyrite electrode. Since pyrite is a semiconductor, the system $Fe(OH)_k{}^{(n-k)+}/FeS_2$ can be considered to be a hydroxy sulfide/metallic electrode whose potential can be defined by

$$E = E^{\circ}_{ox} + \frac{RT}{nF} \ln a_{ox} a^k_{H_3O^+} \quad (3)$$

where

$$ox = Fe(OH)_k{}^{(n-k)+}/FeS_2$$

If only solid components are formed in the layer near the electrode, the expression for the potential of the pyrite electrode can be simplified:

$$E = E^{\circ}_{ox} + \frac{RT}{nF} \ln a^{k}_{H_3O^+} \quad (4)$$

From expression (4) it can be seen that the potential of a pyrite electrode depends on the activity of H_3O^+ ions. Eq. (4) 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 dilute aqueous solution, the activity of the water would be constant, but if the Nernst equation is applied in non-aqueous solution, the potential developed would be related to the activities of both the hydrogen ions and the water [12].

$$E = E^{\circ} + \frac{RT}{nF} \ln[a_{H_3O^+}/(a_{H_2O})^{1/2}] \quad (5)$$

When a solution of quaternary ammonium hydroxide (TBAH) in non-aqueous solvents is used as the titrant, water is formed 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.

3.2. Slopes of the potential response of the pyrite pH sensor

The values of the slope of the potential in *N,N*-dimethylformamide for a given range of concentrations is 39.0 mV, while for methylpyrrolidone it is 45.0 mV (Figs. 3 and 4). Since the pyrite electrode exhibits a sub-Nernst dependence, it cannot be used for the measurement of pH of the solution, but since the potential of a pyrite electrode as an indicator electrode is very stable with respect to time (Fig. 2), it can be successfully applied to the titration of acids in *N,N*-dimethylformamide, methylpyrrolidone and pyridine as solvent.

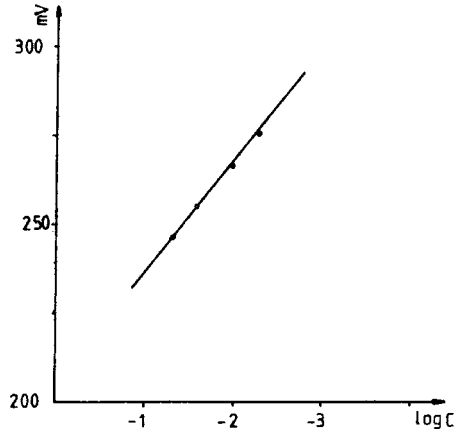

Fig. 3. Plots of the pyrite electrode potential versus log c (concentrations) *p*-toluene-sulfonic acid in *N,N*-dimethylformamide.

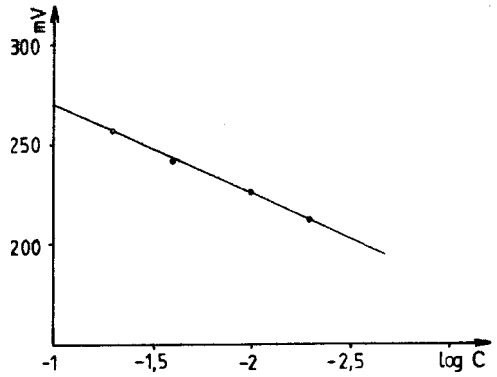

Fig. 4. Plots of the pyrite electrode potential versus log c (concentrations) *p*-toluol-sulfonic acid in methylpyrrolidone.

3.3. Titration of acids in N,N-dimethylformamide, methylpyrrolidone and pyridine

The behavior of a pyrite electrode as an indicator electrode was checked by the titration of a series of organic acids of different strengths and various structures. The titration was carried out by using sodium methylate, KOH in methanol or tetrabutylammonium hydroxide, the concentration of which had been determined with benzoic acid before the titrations.

The titrations of acids in methylpyrrolidone with sodium methylate can be represented by the following equations:

$$C_5H_9ON + HA \rightleftarrows C_5H_9ONH^+ + A^-$$

$$CH_3ONa \rightleftarrows CH_3O^- + Na^+$$

$$C_5H_9ONH^+ + CH_3O^- \rightleftarrows C_5H_9ON + CH_3OH$$

$$Na^+ + A^- \rightleftarrows NaA$$

Summary:

$$HA + CH_3ONa \rightleftarrows CH_3OH + NaA \quad (6)$$

And with TBAH by:

$$C_5H_9ON + HA \rightleftarrows C_5H_9ONH^+ + A^-$$

$$R_4NOH \rightleftarrows R_4N^+ + OH^-$$

$$C_5H_9ONH^+ + OH^- \rightleftarrows C_5H_9ON + H_2O$$

$$C_5H_9ON^+ + A^- \rightleftarrows R_4NA$$

Summary:

$$HA + R_4NOH \rightleftarrows R_4NA + H_2O$$

As it can be seen from the above equations, while titrating an acid with TBAH, water, which has negative effects

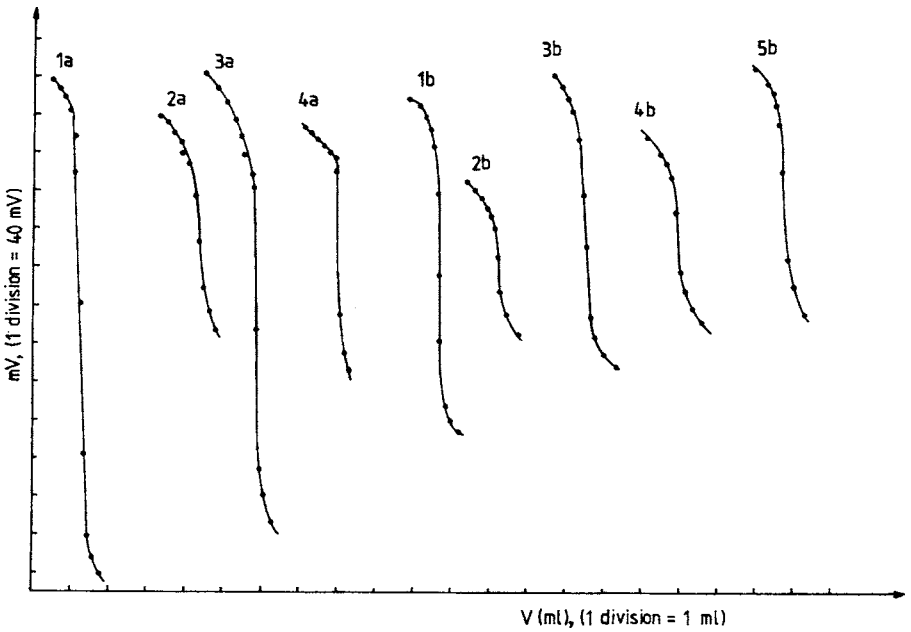

Fig. 5. The effect of the indicator electrode on the shape of the end-point inflexion in the potentiometric titration of benzoic acid and α-nitroso-β-naphthol in methylpyrrolidone: 1a, 2a, 1b, 2b: glass electrode; 3a, 4a, 3b, 4b, 5b: FeS2-electrode. Titrant: 1a, 1b, 3b: TBAH; 2a, 3a, 5b: sodium methylate; 4a, 2b, 4b: potassium hydroxide.

on the titration of weak acids with this titrant, is released. The curves of the titration of various organic acids in methylpyrrolidone as the solvent are shown in Fig. 5. The curves of the titrations in dimethylformamide are shown in Fig. 6. and the curves of the titration in pyridine as the solvent with sodium methylate and the application of KOH in methanol and TBAH in a mixture of methanol and 2-propanol as titrants with the application of the electrode couples FeS_2–SCE and glass–SCE are shown in Fig. 7. While titrating benzoic acid, for example, the potential jumps at the TEP ranges from 210–311 mV/0.3 mol when a pyrite electrode is used as the sensor and 116–352 mV mL^{-1} when a glass electrode is used (Table 1). When sodium methylate and TBAH are used as titrants, the same jumps are obtained while applying pyrite as the sensor. If a TEP glass electrode is used for the detection, the potential jumps are

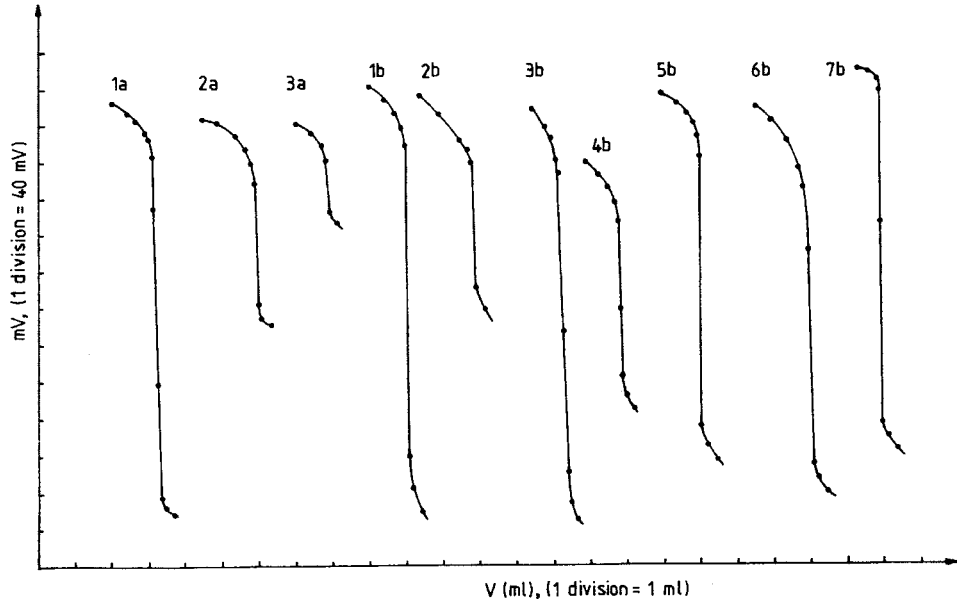

Fig. 6. The effect of the indicator electrode on the shape of the end-point inflection in the potentiometric titration of acids in *N,N*-dimethylformamide: 1a, 2a, 3a-benzoic acid (glass electrode), 1b, 2b-benzoic acid (FeS_2 electrode); 3b, 4b-α-nitroso-β-naphthol (FeS_2 electrode); 5b-anthranylic acid (FeS_2 electrode); 6b-malonic acid (FeS_2 electrode); 7b-salicylic acid (FeS_2 electrode). Titrant: 1a-TBAH; 3a, 1b, 3b, 5b, 6b, 7b: sodium methylate; 2b, 4b-KOH.

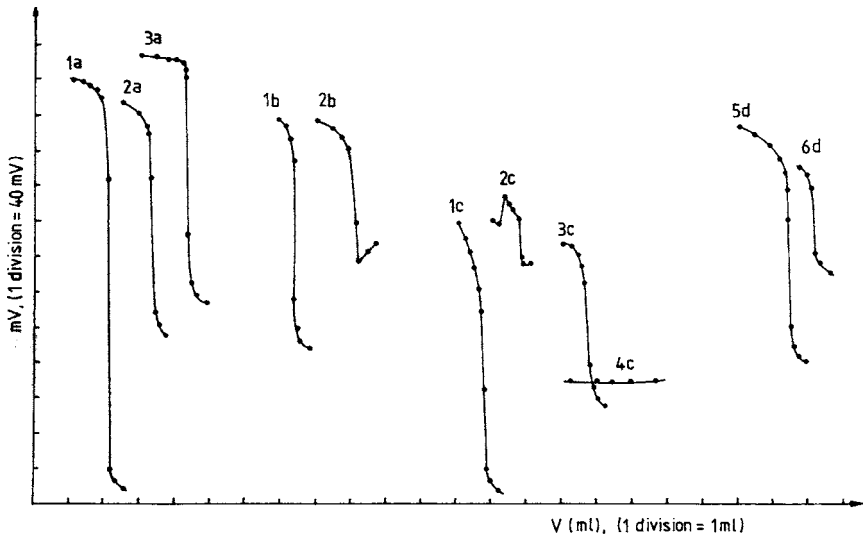

Fig. 7. The effect of the indicator electrode on the shape of the end-point inflection in the potentiometric titration of acids in pyridine: 1b, 2b, 4c: glass electrode; 1a, 2a, 3a, 1c, 2c, 3c, 5d, 6d: FeS2 electrode. Titrant: 2a, 1c: TBAH; 1a, 2b, 3c, 4c, 6d: sodium methylate; 3a, 1b, 2c, 5d: KOH.

decreased when sodium methylate is applied as the titrant due to the effect of sodium ions on the glass electrode.

While titrating α-nitrose-β-naphthol with pyrite as the sensor, the potential jumps were the same irrespective of whether TBAH or sodium methylate is used, but they were slightly decreased when KOH was applied. When a glass electrode was applied in the titration of this compound, the potential jumps are much

Table 1
Potential changes at the titration end-point in the potentiometric determination of acids in pyrrolidone and pyridine

Titrated compound	Solution	Titrating agent	Potential jump in mV	
			FeS_2–SCE	Glass–SCE
Benzoic acid	*N*,*N*-dimethylformamide	TBAH[a]	–	325
		Potassium hydroxide	191	156
		Sodium methylate	359	69
α-Nitroso-β-naphthol	*N*,*N*-dimethylformamide	Potassium hydroxide	177	
		Sodium methylate	317	
Malonic acid	*N*,*N*-dimethylformamide	Sodium Methylate	293	
		Potassium hydroxide		
Salicylic acid	*N*,*N*-dimethylformamide	Sodium methylate	375	
		Potassium hydroxide	276	
Anthranylic acid	*N*,*N*-dimethylformamide	Sodium methylate	288	
		Potassium hydroxide	173	
Benzoic acid	Pyrrolidone	TBAH[a]	321	352
		Potassium hydroxide	210	
		Sodium methylate	310	116
α-Nitroso-β-naphthol	Pyrrolidone	TBAH[a]	170	200
		Potassium hydroxide	145	89
		Sodium methylate	170	60
Palmitic acid	Pyrrolidone	TBAH[a]	151	–
		Sodium methylate	173	–
		Potassium hydroxide	188	–
Salicylic acid	Pyrrolidone	Sodium methylate	174	
		Potassium hydroxide	199	
Anthranylic acid	Pyrrolidone	Sodium methylate	121	
		Potassium hydroxide	185	
α-Nitroso-β-naphthol	Pyridine	TBAH[a]	266	
		Potassium hydroxide	186	
Anthranylic acid	Pyridine	TBAH[a]	216	
		Sodium methylate	365	
		Potassium hydroxide	154	
Salicylic acid	Pyridine Sodium	Methylate	331	

[a] Tetrabutylammonium hydroxide.

lower when sodium methylate was applied than with TBAH.

While titrating in *N*,*N*-dimethylformamide with pyrite as the sensor, the highest potential jumps were obtained when sodium methylate was applied as the titrant (288–377 mV/0.3 mL). If KOH was applied in the titration, the potential jumps were lower, ranging from 173–276 mV/0.3 mL. In the titration of benzoic acid with a glass electrode as the indicator, the smallest jumps were obtained in this solvent with sodium methylate.

In the titration in pyridine with pyrite as the sensor, the highest potential jumps were obtained when sodium methylate was applied as the titrant. Thus, while titrating anthranylic acid with TBAH a jump of 216 mV/0.3 mL was obtained and while titrating the same acid with KOH and sodium methylate, jumps of 154 mV/0.3 mL and 365 mV/0.3 mL, respectively, were obtained. While titrating α-naphthol with TBAH a jump of 190 mV/0.3 mL was obtained and while titrating α-naphthol with sodium methylate and KOH, jumps of 150 mV/0.3 mL and 60 mV/0.3 mL, respectively, were obtained. When the titration was carried out with sodium methylate using a glass electrode, no jump was observed.

When the pyrite electrode was applied as an indicator electrode in pyrrolidone, *N*,*N*-dimethylformamide and pyridine the potential in the course of titration and at the equivalence point (TEP) were found to be rapidly established (within a few minutes) and the change of the potential at the TEP coincided with the change of the applied indicator colour.

Water lowers the potential jumps at the TEP in all the applied solvents. The anthranylic acid titration curves in pyridine at different concentrations of water are shown in Fig. 8. If the solvent contains less than 0.1% of water, the potential jump at the TEP to 148 mV/0.3 mL. If 1% or 10% of water was present, the jumps were 88 mV/0.3 mL and 80 mV/0.3 mL, respectively. The greatest decrease of potential jump was obtained if the content of water was increased by 0.5%. Since water is released in the course of the titrations of acids when applying TBAH (reaction 9), it is the best to use sodium methylate as the titrant.

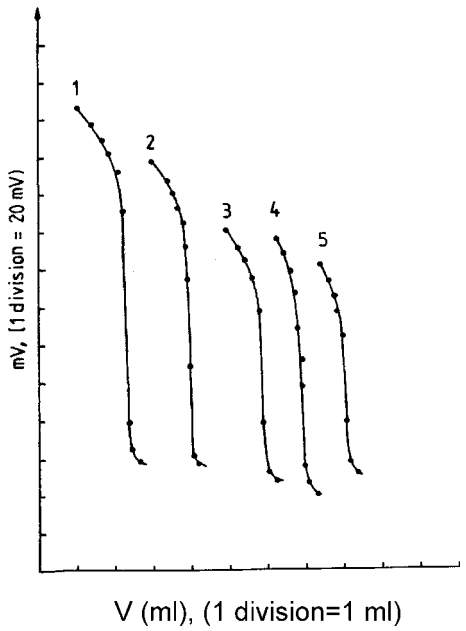

Fig. 8. Potentiometric titration curves of anthranylic acid in pyridine obtained by using a pyrite electrode as indicator electrode and KOH as titrant: 1: non-aqueous media; 2: 0.5% water; 3: 1% water; 4: 5% water; 5: 10% water.

The results obtained in the determination of investigated acid (Table 2) in pyrrolidone, pyridine and *N*,*N*-dimethylformamide, using a pyrite indicator electrode deviated on average by ±0.1–0.35% from those obtained with a glass electrode.

Table 2
Potentiometric titration of acids in non-aqueous solution by the application of the electrode pairs FeS_2–SCE

Titrated	Solvent	Number of determinations	Taken (mg)	Found (%)
Benzoicacid	Methylpyrrolidone	6	24.42	100.00 ± 0.2[a]
α-Nitroso-β-naphthol	Methylpyrrolidone	4	17.32	99.70 ± 0.4[a]
Salicylic acid	Methylpyrrolidone	6	23.18	99.80 ± 0.2[a]
Palmitic acid	Methylpyrrolidone	5	16.23	99.68 ± 0.3[a]
Anthranylic acid	Methylpyrrolidone	6	23.20	99.72 ± 0.1[a]
Anthranylic acid	*N*,*N*-dimethylformamide	5	23.37	98.01 ± 0.7[b]
Salicylic acid	*N*,*N*-dimethylformamide	5	16.92	99.74 ± 0,1[b]
Salicylic acid	*N*,*N*-dimethylformamide	6	16.92	99.65 ± 0,1[a]
α-Nitroso-β-naphthol	*N*,*N*-dimethylformamide	6	26.88	98.98 ± 0.66[b]
α-Nitroso-β-naphthol	*N*,*N*-dimethylformamide	5	26.88	99.59 ± 0.1[a]
Malonic acid	*N*,*N*-dimethylformamide	5	17.68	99.74 ± 0.11[a]
α-Nitroso-β-naphthol	Pyridine	4	24.12	99.50 ± 0.7[b]
α-Nitroso-β-naphthol	Pyridine	4	24.12	99.53 ± 1.0[a]
Anthranylic acid	Pyridine	4	19.64	99.65 ± 0.6[b]
Salicylic acid	Pyridine	4	19.39	98.88 ± 0.5[b]
Benzoic acid	Pyridine	3	22.60	99.65 ± 0.37[b]
Benzoic acid	Pyridine	3	22.60	100.11 ± 0.2[a]

[a] Titration with sodium methylate.
[b] Titration with KOH in methanol.

4. Conclusion

The obtained results show that a pyrite electrode can be successfully applied as an indicator electrode in the potentiometric titration of weak acids with standard solutions of bases (KOH, sodium methylate and TBAH) in pyrrolidone, pyridine and *N*,*N*-dimethylformamide as solvents.

The potential in the course of the titration and at the equivalence point (TEP) was found to be rapidly established.

Sodium methylate, potassium hydroxide and tetrabutylammonium hydroxide were proved to be a very suitable titrating agent for these titration.

The results obtained in the determination of the investigated acids using a pyrite indicator electrode deviated from those obtained using a glass electrode on average by ±0.1–0.35%.

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