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Original scientific paper

Coulometric titrations of bases in propylene carbonate and γ-butyrolactone using hydroquinone as the depolarizer and a quinhydrone indicator electrode

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The application of hydroquinone for the coulometric generation of hydrogen ions in propylene carbonate (PC) and γ-butyrolactone (GBL) is described. The current-potential curves recorded for this depolarizer, titrated bases, indicator and the solvents used showed that the investigated depolarizer is oxidized at lower potentials than the oxidation potentials of other components in the solution. The hydrogen ions generated by the oxidation of hydroquinone were used for the titration of organic bases (triethylamine, *n*-butylamine, pyridine, quinoline, aniline, *N,N'*-diphenylguanidine, piperidine, and 2,2' -bipyridine) in PC and GBL with with visual (Crystal Violet as indicator) and potentiometric end-point detection using a quinhydrone electrode as the indicator electrode. The quinhydrone added to the to be analyzed solution served both as a source of hydrogen ions and, together with the immersed platinum electrode, as a quinhydrone electrode. The relative error of the determination of the bases was about 1 %.

Keywords: propylene carbonate, γ-butyrolactone, coulometric titrations, hydroquinone, base, quinhydrone electrode.

INTRODUCTION

From the analytical poit of view propylene carbonate (PC) and γ-butyrolactone (GBL) have some advantages for acid-base titrations over other protophobic solvents, like acetonitrile or acetone.[1]

PC (4-methyl-1,3-dioxolan-2-one) is an aprotic dipolar solvent with a high relative permittivity (64.4 at 298.15 K), a dipole moment of 4.94 D (298.15 K) and a relatively large acidity scale (29 pK_{SH} scale). Most organic compounds are soluble in this solvent. Its high relative permittivity permits ionic salts to dissolve at concentrations of several moles per liter. PC has a wide liquid range (218.62 to 515.15 K), it is colorless, odorless, nontoxic, and is not appreciably hygroscopic. Its principal disadvantages are that it has a moderately high viscosity (2.5 cP) and that it hydrolyzes fairly rapidly in the presence of strong acids or bases. Standard solutions of strong acids are not stable in PC, as is also the case with acetonitrile and acetone.

However, the concentration of dilute solutions of strong acids obtained from freshly prepared stock solutions remain constant for 4 h. On accout of these properties, PC has been recommended by Baranov *et al.*[2] as a medium for the titration of acids and bases. Since solutions of perchloric acid in PC are unstable, potentiometric titration of organic bases in this solvent are carried out by using a solution of perchloric acid in PC–methanol (5+1, v/v) as the titrant and a glass electrode as the indicator electrode. Izutsu and co-workers[3] determined the dissociation constants of some protonated amines in PC.

In our previous papers,[4–6] it was shown that the difficulties encountered in the classical titrations of bases is PC can be avoided by using coulometry; the titrations of bases being carried out with hydrogen ions obtained by the anodic oxidation of ascorbic acid, esters of gallic acid, pyrocatechol and pyrogallol on a platinum anode and hydrogen dissolved in palladium. For potentiometric end-point detection glass, an antimony, hydrogen/palladium electrode and a platinum electrode were used as the indicator electrode. L' Her and Courtat-Coupez[7] investigated the behaviour of a hydrogen electrode in PC. Izutsu and co-workers[8] found that a glass electrode becames somewhat erratic at pH<5 and at high pH values.

GBL (tetrahydro-2-furanon) is a dipolar aprotic solvent with a reltive permittivity of 41.6 (298.15 K), a dipole moment of 3.97 D (298.15 K), a wide liquid range (229.62 to 477.15 K) and a relatively large acidity scale (about 30 on the pK_{SH} scale). Although this solvent posseses properties characteristic of a good solvent for electrochemical investigations and acid-base determinations, only few data on acid-base behaviour in GBL have been reported in the literature. Coetzee *et al.*[9] reported on the potentiometric characterization of GBL using ion-selective electrodes. Izutsu and co-workers[10] determined the dissociation constant of some acids and protonated bases in GBL and the obtained pK_a values were compared with those in PC; the average difference between the the pK_a values in the two solvents was 0.96. This result supports the fact that the acid-base property of GBL is close to that of PC. No data have been reported on the application of GBL as a solvent for the coulometric determinations of bases.

Taking into account all the good properties of PC and GBL as media for the titration of bases, as well as the advantages of coulometry, in this work we investigated the possibility of coulometric determinations of bases in PC and GBL, using hydroquinone as the anodic depolarizer and a quinhydrone indicator electrode for potentiometric end-point detection.

EXPERIMENTAL

Reagents

All chemicals were of analytical reagent grade from Merck and Fluka. PC and GBL were used without purification. The liquid bases were first dried over fused potassium hydroxide and then distilled under reduced pressure. Solutions of bases were used as primary standards or their concentrations were previously determined coulometrically.[6]

The supporting electrolyte was 0.1 mol/dm^3 sodium perchlorate in PC and GBL. For visual end-point detections in PC and GBL, a 0.1 % solution of Crystal Violet in these solvents was used.

The volumes of bases were measured by means of a microburette with a PTFE tip; for the visual end-point detection 1.00 cm^3 of the investigated bases were measured, whereas for the potentiometric end-point detection 2.00 – 3.00 cm^3 of bases were used.

Apparatus

The apparatus for the coulometric titration of bases with visual end-point detection has been described previously.[11]

The apparatus used for the coulometric-potentiometric titrations is shown in Fig. 1.

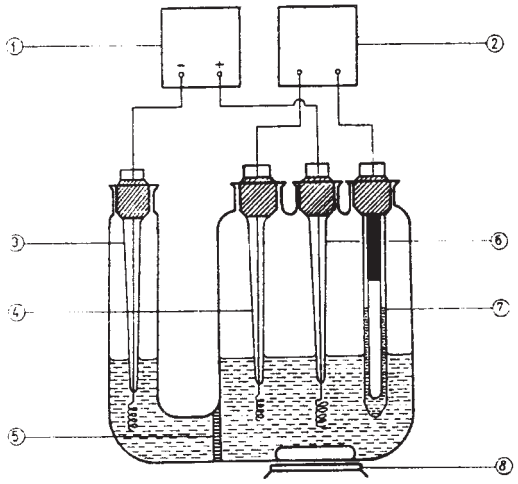

Fig. 1. Schematic diagram of the apparatus for coulometric titration: 1) current stabilizer; 2) pH-meter; 3) Pt-cathode; 4) Pt-indicator electrode; 5) G-4 sintered-glass disk; 6) Pt-anode; 7) SCE and 8) magnetic stirrer.

The current source was an STNS 50260 current stabilizer (Vinča, Belgrade) and the current in the generator circuit was measured with a precise milliammeter (Iskra, Kranj). The volume of the anolyte was 20 cm^3 and that of the catholyte 5 cm^3. The cathode and anode were platinum wire spirals each with a surface area of 27 mm^2. The indicator electrode was a quinhydrone electrode, consisting of a platinum wire of 50 mm^2 area immersed in the titrated solution saturated with quinhydrone. The reference electrode was a modified saturated calomel electrode (SCE) containing methanolic potassium chloride solution. The potentials during the course of the titration were measured with a pH-meter MV 870 Original pH Messgerat.

Procedure

Visual end-point detection. The procedure for coulometric titration of bases with visual end-point detection has been described in an earlier paper.[4]

Potentiometric end-point detection. The supporting electrolyte was poured into the cathode and anode compartments of the electrolyte vessel up to the same level. The platinum cathode was dipped into the catholyte and, after the addition of about 100 mg hydroquinone and 100 mg quinhydrone, the platinum anode, platinum wire and SCE were immersed in the anolyte. A weighed amount of the base to be determined was added to anolyte and the current was then switched on; hydrogen ions were generated discontinuously and the indicator electrode potentials were read on the pH-meter. The titration end-point was determined from the second derivative.

RESULTS AND DISCUSSION

It has been shown[10–14] that hydroquinone can be used as an anodic depolarizer in the coulometric titrations of bases in some dipolar aprotic solvents (acetonitrile and acetone).

In order to check the possibility of applying the hydrogen ions obtained by the anodic oxidation of hydroquinone for the titration of organic bases in PC and GBL, the current-potential curves for the supporting electrolyte, indicator, titrated base and hydroquinone were first recorded. The current-potential curves recorded for the supporting electrolyte in PC and GBL, titrated bases, indicator and hydroquinone (Fig. 2) show that hydroquinone is oxidized at a more negative potential than the oxidation potentials of the other components present in the solution.

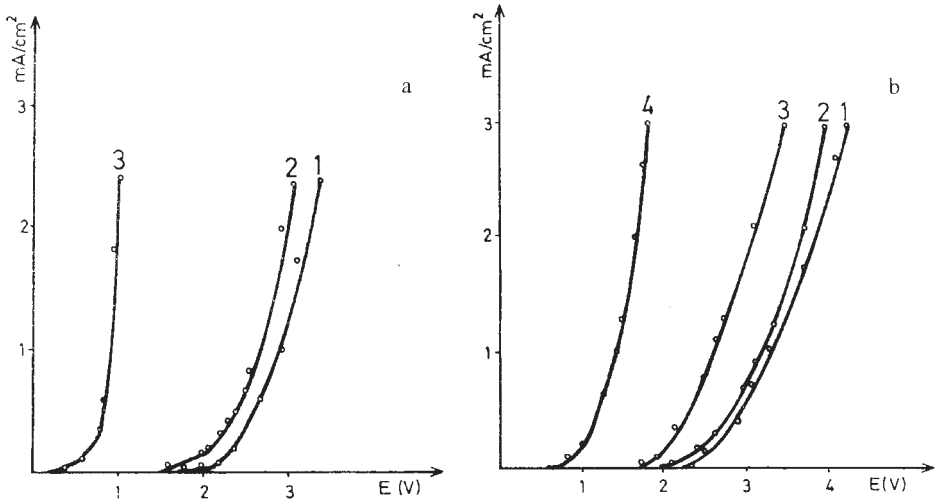

Fig. 2. Dependence of the current density on the potential at the platinum anode in 0.1 mol/dm^3 solution of sodium perchlorate in PC a) and GBL b). Curves: a) 1) PC; 2) pyridine; 3) hydroquinone; b) 1) GBL; 2) indicator; 3) pyridine and 4) hydroquinone.

The hydrogen ions generated at the platinum anode were used for the titration of organic bases (triethylamine, *n*-butylamine, pyridine, quinoline, aniline, *N,N'*-diphenylguanidine, piperidine and 2,2'-bipyridine) in PC and GBL with visual and potentiometric end-point detection.

Visual end-point detection. Nedvetskaya *et al.*[15] determined the dissociation constants of Methyl Orange, Methyl Red, Bromophenol Blue, Bromothymol Blue and Thymol Blue potentiometrically and spectrophotometrically in PC. These indicators were recommended for the visual titration of strong bases, salts and weak acids in PC. Our investigations showed that, in addition to these, Crystal Violet can also be used for the visual end-point detection in coulometric titrations of bases in PC and GBL. A sharper end-point is obtained with Crystal Violet than with the other indicators.

The results of the coulometric titrations of bases with hydrogen ions obtained by the oxidation of hydroquinone in PC and GBL (Table I) indicate that the current efficiency was 100 %.

Potentiometric end-point detection. For the end-point detection in potentiometric titrations of acids and bases in nonaqueous solvents different metal indicator electrodes were used. A platinum electrode is unsuitable for the measurement of

the acidity of a solution since it is not fully reversible; its potential is dependent on time and the results are not reproducible. Vajgand *et al.*[16,17] showed that the addition of quinhydrone, which reacts reversibly in acid media, eliminates this disadvantage of the Pt-electrode in some nonaqueous solvents. They applied two polarized qyinhydrone electrodes for bipotentiometric and biamperometric end-point detection in the coulometric titrations of bases in acetic acid and acetic anhydride.

In our previous work[5] the titrations of acids and bases in PC were carried out with a platinum electrode which had been previously cathodically or anodically polarized, or activated by various chemicals. The anodically polarized platinum electrode showed higher potentials at the equivalence point than other metallic electrodes but required successive polarization after each titration.

In order to avoid the activation of the platinum electrode, a quinhydrone electrode as indicator electrode was applied in coulometric-potentiometric titrations of bases in PC and GBL. The quinhydrone added to the to be analysed solution served both as the source of hydrogen ions and, together with an immersed platinum electrode, as a quinhydrone electrode.

The titration curves for triethylamine, *n*-butylamine, 2,2'-bipyridine, pyridine and *N,N'*-diphenylguanidine in PC and triethylamine and *N,N'*-diphenylguanidine in GBL are shown in Fig. 3.

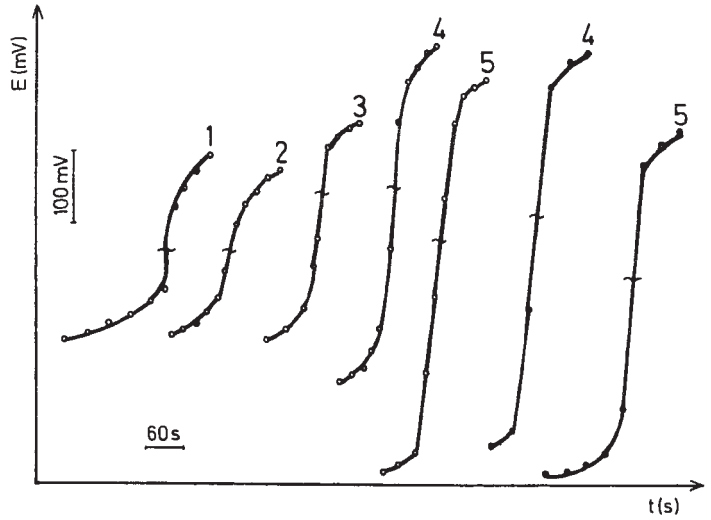

Fig. 3. Coulometric-potentiometric titration curves for bases in PC (ooo) and GBL (•••): 1) pyridine; 2) *n*-butylamine; 3) 2,2'-bipyridine; 4) *N,N'*-diphenylguanidine and 5) triethylamine.

In the titration of strong bases (triethylamine and *N,N'*-diphenylguanidine) in PC and GBL the potential jump at the equivalence point is about 300 mV (for base concentrations in the range from 0.0001 to 0.001 mol/dm^3). In the titration of weak bases (aniline and *n*-butylamine) in PC the potential change at the end-point is about 100 mV. The titration of weak bases in GBL is unsatisfactory because there is no sharp inflection at the equivalence point. The reason for this probably lies in the fact

that GBL is somewhat more basic than PC. The titration of very weak bases (urea) in PC and GBL is not possible.

The potentials during the course of the titration and at the equivalence point were established rapidly.

The results of the coulometric titrations of bases in PC and GBL obtained using hydroquinone as depolarizer and a quinhydrone indicator electrode (Table I) show that the relative error of the determination is about 1 %.

TABLE I. Results of the coulometric titrations of bases in PC and GBL with hydrogen ions generated by the oxidation of hydroquinone with visual and potentiometric end-point detection. Supporting electrolyte 0.1 mol/dm^3 $NaClO_4$. Electrode pair: qyinhydrone electrode - modified SCE. I = 0.010 A

Solvent	Titrated base	Taken/mg	Number of determination	Found/%
Visual end-point detection,				
Propylene carbonate	Triethylamine	2.20	3	99.9 ± 0.1
	n-Butylamine	4.33	6	100.1 ± 0.5
	Pyridine	2.49	7	100.1 ± 0.2
	Quinoline	3.64	7	100.0 ± 0.6
γ-Butyrolactone	*N,N'*-Diphenylguanidine	4.82	8	99.9 ± 0.4
	Triethylamine	3.84	6	99.8 ± 0.2
	Piperidine	3.37	6	100.2 ± 0.2
Potentiometric end-point detection				
Propylene carbonate	Triethylamine	16.50	6	100.2 ± 0.4
	Pyridine	22.33	6	99.6 ± 0.1
	2.2'-Bipyridine	21.60	5	99.2 ± 0.5
	n-Butylamine	12.26	6	100.8 ± 0.4
	Aniline	18.60	5	99.9 ± 0.8
	N,N'-Diphenylguanidine	15.77	3	100.5 ± 0.3
γ-Butyrolactone	Triethylamine	5.97	5	100.2 ± 0.7
	N,N'-Diphenylguanidine	14.15	6	99.9 ± 0.7

On the basis of these results it may be concluded that the oxidation of hydroquinone in propylene carbonate and γ-butyrolactone as solvents, proceeds with a 100 % current efficiency and that the generated hydrogen ions can be applied for the determination of bases. By using quinhydrone indicator electrode it is possible to eliminate the otherwise required activation of platinum electrode.

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ИЗВОД

КУЛОМЕТРИЈСКЕ ТИТРАЦИЈЕ БАЗА У ПРОПИЛЕНКАРБОНАТУ И γ-БУТИРОЛАКТОНУ ПРИМЕНОМ ХИДРОХИНОНА КАО ДЕПОЛАРИЗАТОРА И ХИНХИДРОНОВЕ ИНДИКАТОРСКЕ ЕЛЕКТРОДЕ

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Испитана је примена хидрохинона за кулометријско генерисање водоничних јона у пропиленкарбонату (PC) и γ-бутиролактону (GBL). Криве струја-потенцијал снимљене за овај деполаризатор, титроване базе и употребљене растваре показују да се испитивани деполаризатор оксидује на нижем потенцијалу од потенцијала оксидације других компонената у раствору. Водоничним јонима добијеним оксидацијом хидрохинона титроване су органске базе (триетиламин, *n*-бутиламин, пиридин, хинолин, анилин, *N,N'*-дифенилгванидин, пиперидин и 2,2′-бипиридин) у PC и GBL са визуелним (кристалвиолет као индикатор) и потенциометријским детектовањем завршне тачке титрације употребом хинхидронове индикаторске електроде. Хинхидрон који се додаје у испитивани раствор служи као извор водоничних јона, и заједно са уроњеном платинском електродом, чини хинхидронову електроду. Релативна грешка одређивања база је око 1 %.

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