

ACID-BASE TITRATIONS WITH TWO POLARIZABLE ELECTRODES

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Dedicated to honour the memory of Professor J. Hanuš on the occasion of the centenary of his birthday.

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The use of a pair of platinum or glassy carbon electrodes for biamperometric, bipotentiometric, and a.c. polarization aqueous acid-base titrations has been studied. The shape of the titration curves has been explained on the basis of the pH dependence of the polarization curve of the irreversible system of water oxidation-dissolved oxygen reduction. It has been shown that these titrations are sufficiently accurate and precise and are suitable even for the direct determination of very weak acids (*e.g.* boric) or bases in aqueous solutions. The advantage of these methods over equilibrium potentiometric titrations is that the measured value is almost instantaneously stable and that even very low acid or base concentrations can be titrated (down to $10^{-5}N$ in favourable cases using a.c. polarization end-point detection).

Platinum and glassy carbon indication electrodes were used for equilibrium potentiometric acid-base titrations in our previous paper¹. The shape of the titration curves obtained was explained using the polarization curves of the titration systems measured. The accuracy and precision of these determinations were satisfactory, the disadvantages being that the potential values stabilized slowly in the vicinity of the end-point and that more dilute solutions than about $10^{-3}N$ could not be satisfactorily titrated. Hence, biamperometric, bipotentiometric, and a.c. polarization end-point detections using a pair of similar platinum or glassy carbon electrodes are dealt with in the present paper since it may be assumed that these methods will be more sensitive and that the measured values will stabilize more rapidly.

The methods of acid-base titrations with two polarizable electrodes which have been reported in the literature either use electrodes responding directly to the pH of the solution (*e.g.* antimony or bismuth) or platinum electrodes with an electrometric indicator (*e.g.* hydrogen peroxide, quinhydrone, *etc.*). For references see *e.g.* a recent review². In the present paper, the pH dependence of the irreversible system of water oxidation-dissolved oxygen reduction is utilized so that no electrometric indicator is necessary.

EXPERIMENTAL

Reagents and Apparatus

All acids and bases used were the products of Lachema, Czechoslovakia, of reagent grade purity. Carbonate-free solutions of sodium hydroxide were prepared by ion exchange on the Merck III

strongly alkaline anion exchanger in the OH^- form. All the solutions were standardized using oxalic acid and oxalate as standards.

The apparatuses for biamperometric and bipotentiometric titrations were arranged in the usual way (see Figs 1 and 2 in the review²). A 4 V battery was used as a source of applied voltage in biamperometric titrations and the current was measured with the galvanometer „Titroskop“ (Laboratorní přístroje, Czechoslovakia) with a sensitivity of $9 \cdot 10^{-9}$ A/scale div. The E 456 Polarizer (Metrohm, Switzerland) served as a source of constant current in bipotentiometric titrations and the potential differences were measured with the Multoscop V pH-meter (Laboratorní přístroje, Czechoslovakia). The a.c. polarization titrations³ were carried out with the simplified two-electrode system devised by Kitagawa⁴ using a commercial apparatus, Konduktoskop E 365 B (Metrohm, Switzerland) with a frequency of 50 Hz and a current density of about $1 \mu\text{A}/\text{mm}^2$. In order to compare the shape of titration curves with that predicted from the course of polarization curves, the potentials of the indicator electrodes were measured during the titrations using two saturated calomel electrodes with Luggin capillaries approaching closely the surface of the electrodes. The experimental arrangement in this case was similar to that described in a previous paper⁵. The indicator electrodes used were two platinum wires with a diameter of 0.5 mm and length 5 mm (surface area of 8.2 mm^2) and two glassy carbon disks (Tokai Electrode Mfg. Co., Nagoya, Japan) with a surface area of 19.6 mm^2 sealed in glass tubes. The platinum electrodes were prepolarized at negative potentials in 0.5M perchloric acid before measurements, the glassy carbon electrodes were polished with alumina. When not in use, the electrodes were stored in distilled water. Polarization curves were recorded with the LP-7 polarograph (Laboratorní přístroje, Czechoslovakia). The pH of solutions was measured with the E 280 A pH-meter (Metrohm, Switzerland). The titrations were performed using a volume of 50 ml of solution, stirred with a magnetic stirrer. All potentials were measured against a saturated calomel electrode.

RESULTS AND DISCUSSION

The potential of the irreversible system, water oxidation-dissolved oxygen reduction, depends approximately on the pH of the solution according to the equations

$$E = \text{const} - 0.059 \text{ pH (platinum)},$$

$$E = \text{const} - 0.020 \text{ pH (glassy carbon)}, \quad (1)$$

where E is the equilibrium potential¹. If both the cathodic and anodic reactions obeyed these equations exactly, there would be no change in the measured signal during titrations with two

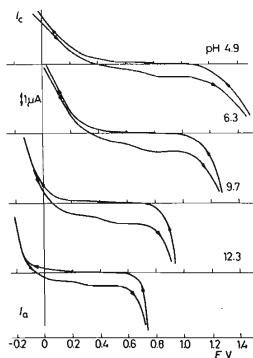


FIG. 1
Polarization Curves of 0.5M Boric Acid at
Various pH Values (adjusted with NaOH)
Platinum rotating wire electrode, 400mV/min.

polarizable electrodes. However, it may be found from the polarization curves of acids measured in various stages of their titration with an alkali that there are several major deviations. *First*, the shift of the voltammetric waves with pH is usually slightly less than the theoretical value (about 50 mV/pH for platinum electrodes, depending on the electrode pretreatment) and the shift of the cathodic wave is usually even less than that of the anodic wave, especially in an alkaline medium (a difference of about 5 mV/pH or more, depending on the electrode pretreatment). *Second*, due to hysteresis, the position of the waves depends upon the direction of polarization: If the potential changes from positive to negative values, the waves are placed at more positive potentials than those with a potential scan from negative to positive values. *Third*, the slope of the anodic and/or cathodic waves increases with increasing pH (the change is especially marked in alkaline solutions). This increase is enhanced in the case of dilute solutions of weak acids by the fact that on their neutralization, dissociated salts are formed and, consequently, the solution electric resistance and the *I.R* drop decrease.

Some typical values of $(\Delta I/\Delta E) \cdot 10^6$ for the electrodes and the pretreatment given are shown in Table I). As an example, the polarization curves of boric acid at a platinum electrode are shown in Fig. 1. The shape of acid-base titration curves will then be determined by the above mentioned factors. Generally, the higher the pH, the higher will be the current in biamperometric titrations, and the smaller the potential difference in bipotentiometric or a.c. polarization titrations. This change is more

TABLE I

Some Typical Values of the Slopes of the Oxygen Reduction and Water Oxidation Waves in Acid for the Given Electrodes and the Given Pre-treatment

Electrode	Acid	pH	$(\Delta I/\Delta E) \cdot 10^6$	
			cathodic	anodic
Pt	boric	0.5M acid	13	16
		6.3	21	30
		9.7	34	92
		12.3	43	128
Pt	hydrochloric	0.1N acid	6.5	16
		1.9	10	16
		4.7	8	16
		11.3	8	27
Pt	acetic	0.1N acid	14	10
		5.3	24	14
		11.6	25	10
C	acetic	0.1N acid	4	8
		5.6	7	9
		11.6	9	8

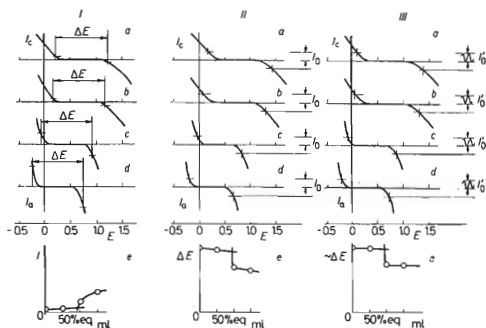


FIG. 2

Method of Constructing Acid-Base Titration Curves with Two Polarizable Electrodes from the Polarization Curves of the Titration Systems: An Acid Titrated with an Alkali

I Biamperometric indication; *II* bipotentiometric indication; *III* a.c. polarization titration. *a* beginning of titration; *b* half titration; *c* end-point; *d* 50% overtitrated; *e* resulting titration curve. ΔE voltage applied; I_0 d.c. current applied; I'_0 a.c. current applied.

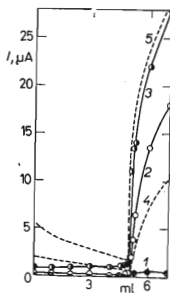


FIG. 3

Biamperometric Titration Curves of 0.1M-HCl Titrated with 0.1M-NaOH at Various Applied Voltages

Platinum electrodes; 1 ΔE 0.75 V; 2 ΔE 1.0 V; 3 ΔE 1.25 V; 4 titration curve predicted from polarization curves for ΔE 1.0 V, 5 titration curve predicted from polarization curves for ΔE 1.25 V.

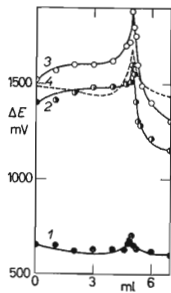


FIG. 4

Bipotentiometric Titration Curves of 0.1M-HCl Titrated with 0.1M-NaOH at Various Applied d.c. Currents

Glassy carbon electrodes; 1 I_0 1 μ A; 2 I_0 5 μ A; 3 I_0 10 μ A; 4 titration curve predicted from polarization curves for I_0 10 μ A.

pronounced in alkaline than in acidic media. A schematic representation of the construction of titration curves from polarization curves is shown in Fig. 2. In practice, titration curves constructed from measured polarization curves reasonably match the measured titration curves.

The effects mentioned would not lead to such sharp changes in the signal measured at the end-point as are encountered in practice. However, there are always differences between the two electrodes in their active surface area, the heterogeneity of the surface etc. which cause somewhat different responses for each electrode and sharper changes of the signal measured at the end-point. Examples of practical curves are shown in Figs 3–7. The effect of the magnitude of the voltage or current applied on the shape of titration curves is obvious from Fig. 2 and practically measured curves are shown in Figs 3 and 4. It is obvious that the greater the differences between the two indicator electrodes, the sharper is the measured signal change at the end-point. Two possible ways of increasing the difference between the electrodes are different pre-treatment of each electrode (confer the differences in polarization curves at different direction of polarization) (Fig. 8) and the use of two electrodes of different sizes (Fig. 9).

A suitably chosen bimetallic pair would, obviously, also yield sharp differential curves as it did in the case of equilibrium potentiometric titrations¹. If *bases are titrated with acids*, the titration

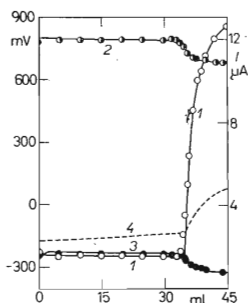


FIG. 5

Biparametric Titration of 0.5M- H_3BO_3 with 0.5M-NaOH

Glassy carbon electrodes; $\Delta E = 1.0 \text{ V}$.
1 Titration curve; 2 potentials of the anode during titration; 3 potentials of the cathode during titration; 4 titration curve predicted from polarization curves.

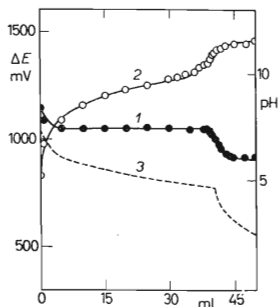


FIG. 6

Bipotentiometric Titration of 0.5M- H_3BO_3 with 0.5M-NaOH

Glassy carbon electrodes; $I_0 = 1 \mu\text{A}$.
1 Titration curve; 2 potentiometric titration curve with a glass electrode; 3 titration curve predicted from polarization curves.

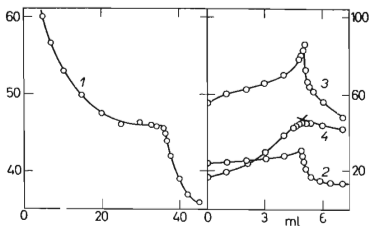


FIG. 7

A.c. Polarization Titration Curves

Platinum electrodes; $I_0 = 10 \mu\text{A}$. 1 35 ml $0.5\text{M-H}_3\text{BO}_3$, sensitivity "3"; 2 5 ml 10^{-2}M-HCl , sensitivity "1"; 3 5 ml 10^{-2}M-HCl , sensitivity "2"; 4 5 ml 10^{-4}M-HCl , sensitivity "3". Titrated with NaOH of the same concentration as the acids titrated. Vertical axis arbitrary units.

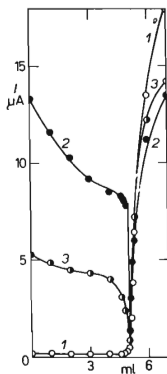


FIG. 8

Biamperometric Titration Curves of 5 ml of 0.1M-HCl with 0.1M-NaOH with Various Electrode Pre-treatments

Platinum electrodes; $\Delta E 1.0 \text{ V}$. 1 Both electrodes polarized cathodically at -2.0 V ; 2 one electrode polarized anodically ($+2.0 \text{ V}$) and the other cathodically (-2.0); 3 both electrodes polarized anodically at $+2.0 \text{ V}$.

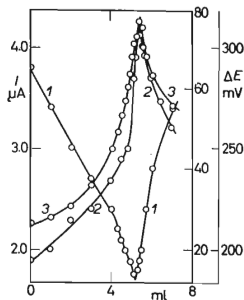


FIG. 9

Titrations of 5 ml of 0.1N-HCl with 0.1N-NaOH Using one Wire Platinum Electrode (8.2 mm^2) and one Foil Platinum Electrode (42.0 mm^2)

1 Biamperometric titration, $\Delta E = 1.0 \text{ V}$; 2 bipotentiometric titration, $I_0 = 1 \mu\text{A}$; 3 a.c. polarization titration, $I_0 = 10 \mu\text{A}$, sensitivity "3". Right hand inner readings arbitrary units.

curves have the opposite shape to that obtained in titrations of acids with bases. Otherwise the sensitivity, accuracy, and precision are identical.

The results of typical practical titrations are summarized in Table II. It has been found that the methods have a higher sensitivity than equilibrium potentiometric titrations. The d.c. methods enabled us to titrate acids and bases down to 10^{-4} M concentration and a.c. polarization titration made possible the titration of 10^{-5} M-HCl with 10^{-5} M-NaOH. It was sufficient to pre-treat the platinum

TABLE II

Comparison of the Accuracy and Precision of the Methods Studied and Equilibrium Potentiometric Titrations with a Glass Electrode

0.1M-HCl, 0.1M-CH₃COOH, and 0.5M-H₃BO₃ titrated with 0.1M or 0.5M-NaOH.

Method	Electrode	K^a	s_4^b	$\bar{x}^c \pm I(0.95)$ M	Relative error, %
Equil. potentiometry	glass	10^{-1}	0.0001	0.1003 ± 0.0003	± 0.29
		10^{-5}	0.0002	0.1001 ± 0.0005	± 0.49
		10^{-10}	0.0025	0.5090 ± 0.0056	± 1.10
	Pt	10^{-1}	0.0006	0.0995 ± 0.0013	± 1.30
		10^{-5}	0.0012	0.1005 ± 0.0026	± 2.58
	Biamperometry	C	10^{-1}	0.0006	0.0995 ± 0.0013
10^{-5}			0.0012	0.1002 ± 0.0026	± 2.59
10^{-10}			0.0042	0.4922 ± 0.0094	± 1.90
Pt		10^{-1}	0.0006	0.1025 ± 0.0013	± 1.26
		10^{-5}	0.0006	0.1015 ± 0.0013	± 1.28
Bipotentiometry		C	10^{-1}	0.0006	0.1009 ± 0.0013
	10^{-5}		0.0006	0.1009 ± 0.0013	± 1.28
	10^{-10}		0.0052	0.4982 ± 0.0114	± 2.29
	Pt	10^{-1}	0.0006	0.0998 ± 0.0013	± 1.30
		10^{-5}	0.0006	0.0992 ± 0.0013	± 1.31
	A. c. Polarization titration	C	10^{-10}	0.0026	0.4989 ± 0.0057
10^{-1}			0.0006	0.1002 ± 0.0013	± 1.30
10^{-5}			0.0017	0.0985 ± 0.0021	± 2.14
10^{-10}		0.0062	0.4968 ± 0.0136	± 2.78	

^a K approx. dissociation constant of acid; ^b s_4 the assessment of standard deviation from four measurements; ^c \bar{x} arithmetical mean (molarity), 95% confidence limits.

electrodes once a day by brief polarization at -2.0 V in dilute perchloric acid, the glassy carbon electrodes worked well after polishing them with alumina before starting to use them and then only rinsing them with distilled water between titrations. It was, of course, necessary to maintain a uniform stirring rate.

As follows from the obtained results, convenient magnitudes for applied signals are 1.0 to 1.4 V in biamperometry, 1.0 to 10.0 μA in bipotentiometry, and about 1 to 10 $\mu\text{A}/\text{mm}^2$ in a.c. polarization titration. Generally, a.c. polarization titration was found to be the most sensitive and precise with the exception of the titration of acetic acid, where biamperometry and bipotentiometry give slightly better results. From the pair biamperometry-bipotentiometry, the latter is generally more precise due to the more favourable shape of the titration curves; an exception is the titration of boric acid, in which biamperometry yields a greater change of the signal measured at the end-point. Platinum electrodes generally show a greater measured signal variation than glassy carbon ones due to the greater effect of pH on the electrode reactions (see equations (1)). Only in the titration of boric acid did the glassy carbon electrodes yield larger current breaks at the end-point of the biamperometric titration.

The stabilization of the measured signal values was instantaneous in a.c. polarization titration, almost instantaneous in bipotentiometric titration, and only in biamperometric titrations was it necessary to wait about 10 to 20 seconds until the value was constant. There is no difference between the signal stabilization of platinum and glassy carbon electrodes. For this reason a.c. polarization titration will definitely find use in automatic acid-base determinations. Its disadvantage is the relatively more complicated apparatus required. An advantage of all these methods is that they do not need reference electrodes and that the electrodes are more robust than the glass electrode; they also make possible the direct titration of hydrofluoric acid.

On the basis of the polarization curves of the titration systems it is possible to predict the optimum value of the applied signal and the approximate shape of the titration curves. Platinum electrodes will probably be more useful in most determinations, but in certain cases glassy carbon ones may yield better results. An advantage of glassy carbon electrodes lies in their simpler pre-treatment and their low cost.

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