

POTENTIOMETRIC TITRATION OF ACIDS AND BASES WITH GRAPHITE MEMBRANE ELECTRODES IN AQUEOUS AND NON-AQUEOUS SOLUTIONS*

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For the end-point detection of acid-base titrations any electrode showing a hydrogen ion function is known to be appropriate. In addition to glass electrodes, hydrogen, quinhydrone or metal—metal oxide electrodes, furthermore molybdenum, tungsten and bright platinum electrodes, which behave as an oxygen-gas electrode, can also be applied for pH measurements.

BERČIK [1] was the first to use graphite electrodes as indicator electrodes in potentiometric acid-base titrations. According to his investigations, carried out with wax-impregnated graphite electrodes [2, 3, 4], this type of electrode is pH-sensitive and its potential change per pH unit as well as the magnitude of the potential jump at the end-point of the titration can be increased if the electrode is "activated", i.e. treated with the solution of different solvents before use. The potential of the electrode, activated with permanganate dissolved in sulphuric acid, changed linearly with the pH, i.e. about 70 mV per pH unit.

According to BERČIK, in the course of the activation process a quinon-hydroquinone redox system is formed, the redox potential of which depends on the pH.

BERČIK and HLADKY [5, 6] as well as BERČIK, ČAKRT and DERZSIOVÁ [7, 8] found wax-impregnated activated graphite electrodes to be convenient for acid-base titrations, both in aqueous and non-aqueous solutions.

MILLER [9] used pyrolytic graphite [10], while DOLEĀL and ŠTULIK [11] applied glassy-carbon electrodes as indicator electrodes in acid-base titrations. According to their results the potential of the pyrolytic graphite electrode changed by 50 mV while that of the glassy carbon electrode by 20 mV per pH unit. DOLEĀL and ŠTULIK found that the presence of anionic oxidants increased the magnitude of the potential jump.

In our present paper we wish to report on our experiments carried out partly with our silicone rubber based graphite electrode [13] which proved to be very useful in voltammetry, partly with electrodes containing—besides

* Dedicated to Prof. L. Telegdy Kováts on the occasion of his 70th birthday.

graphite — also manganese dioxide in different amounts, to investigate whether these electrodes can be used to the detection of the hydrogen-ion concentration.

Experimental

An expanded-scale pH meter (Model OP 205 Radelkis) was used for all measurements. Silicone rubber-based graphite, silicone rubber-based manganese dioxide electrodes and electrodes containing manganese dioxide and graphite together were used as indicator electrodes. The ratio of manganese dioxide to graphite was 25% : 75% and 50% : 50%, respectively. The membrane layer of appropriate composition embedded in silicone rubber was glued to one end of a glass tube. Mercury was poured into the glass tube to ensure electrical contact in all cases. A saturated calomel electrode, and for certain measurements, a silicone rubber-based chloride-selective electrode were used as reference electrodes. In the latter case the concentration of the chloride ions was adjusted originally to a high value.

First the pH sensitivity of the mentioned electrodes was examined. For these studies, calibration curves were obtained in aqueous media, from buffer solutions of different pH values, and titration curves of strong acids and bases as well as of weak acids were recorded.

With consideration of the concentrations of the solutions the titration curves obtained with silicone rubber-based graphite electrode were evaluated on the basis of the correlation between the equilibrium pH values calculated for every point of the titration curve and the mV values measured. The equilibrium pH values were calculated by means of a computer.

Evaluation of both, calibration and titration curves showed the potential of the electrode to change at an average of 30 mV per pH unit.

By soaking the electrodes in a solution of an oxidant for 1 to 3 minutes the value of the potential change increased in dependence of the quality of the oxidant applied [14]. The slope of the pH vs mV function increased significantly when potassium permanganate dissolved in sulphuric acid was used as oxidant. When the electrode was activated with 0,1 N potassium permanganate solution the electrode potential changed at an average value of 60 mV/pH unit, while by using 1 N potassium permanganate solution even a slope of 70 to 90 mV/pH could be obtained.

Numerous potentiometric acid-base titrations were carried out with both non-activated and activated silicone rubber-based graphite electrodes. The measurements were also made by using glass electrodes and classical titration methods and it was found that the end-point of the titrations was correctly indicated by both the activated and non-activated electrodes.

With the activated electrode several titrations can be carried out without further activation, although the pH sensitivity of the electrode decreases from titration to titration [14].

Silicone rubber-based membrane electrodes containing, instead of graphite, manganese dioxide or the mixture of manganese dioxide and graphite in different proportions, are similarly pH-sensitive and can advantageously be used as indicator electrodes in acid-base titrations.

Calibration curves obtained in buffer solutions showed the pH—mV correlation of these electrodes to have an average slope of 60 mV. Though the

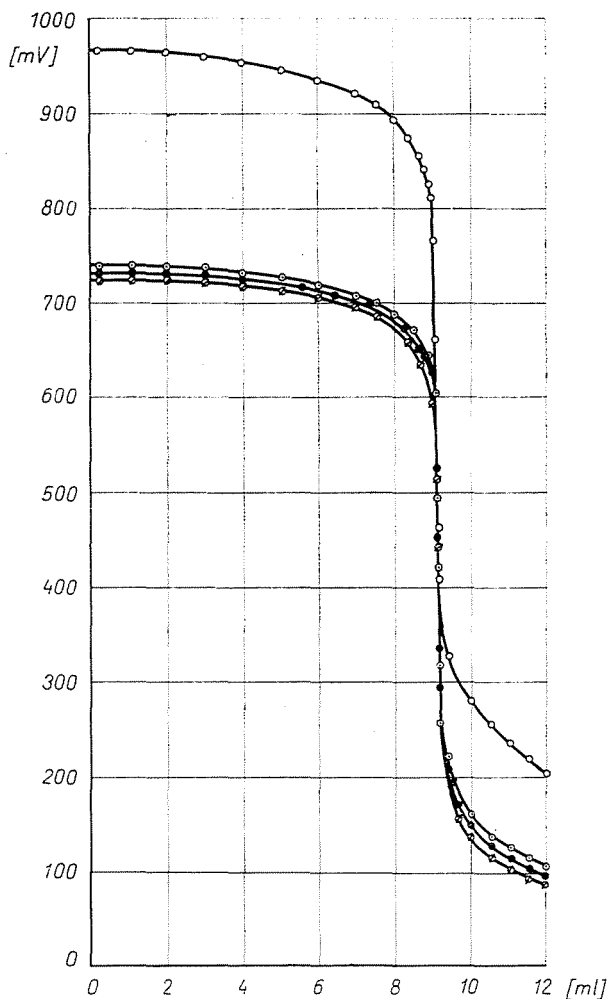


Fig. 1. Titration of 0.100 N HCl with 0.109 N NaOH with silicone rubber-based electrodes of different composition.

magnitude of the potential jump is smaller in the neighbourhood of the equivalence point than for activated graphite electrodes, the values of the electrode potential become very quickly (in a few seconds) constant in the course of the titration, in contrast to activated graphite electrodes where the potential reaches a constant value only in 2—3 minutes. The magnitude of the potential jump does not change even in a longer time-period.

In Fig. 1 the titration curves of hydrochloric acid with sodium hydroxide are shown for silicone rubber-based electrodes of different composition. The membrane of these electrodes consists either of manganese dioxide alone, or of 50% manganese dioxide and 50% graphite, 25% manganese dioxide and 75% graphite, or of activated graphite.

Table I summarizes the results and accuracy of acid-base titrations carried out in aqueous solutions with activated graphite electrode and electrodes containing manganese dioxide in different amounts.

Table I

Results of titrations carried out with silicone rubber-based electrodes containing activated graphite, manganese dioxide, as well as the mixture of manganese dioxide and graphite

Solution titrated	Titrant	Consumed (ml)		Relative error %
		calcd.	found	
0.1 N HCl	0.1 N NaOH	4.20	4.23	+0.71
0.1 N H ₂ SO ₄	0.1 N NaOH	4.20	4.22	+0.47
0.1 N CH ₃ COOH	0.1 N NaOH	2.15	2.15	0.0
0.1 N oxalic acid	0.1 N NaOH	1.544	1.540	-0.26
0.1 N citric acid	0.1 N NaOH	2.149	2.147	-0.09
0.1 N tartaric acid	0.1 N NaOH	2.16	2.15	-0.70
0.1 N nicotinic acid	0.1 N NaOH	3.85	3.85	0.00
0.1 N salicylic acid	0.1 N NaOH	5.33	5.32	-0.19
0.1 N lactic acid	0.1 N NaOH	4.05	4.05	0.00

Experiments were carried out in order to examine whether the electrodes described are suitable to the end-point detection of titrations in non-aqueous media.

To these investigations benzoic acid served as model substance while abs. methanol, abs. ethanol and dimethylformamide were used as non-aqueous solvents. As titrant, potassium hydroxide dissolved in abs. methanol was applied. The content of the non-aqueous solvent in the solution to be titrated varied between 50 and 100% v/v.

It was established that the end-point of the titrations was correctly detected by every electrode type but in using electrodes containing, beside gra-

phite, also manganese dioxide, the potential values significantly faster stabilized in the course of the titration than in the case of an activated electrode.

The graphite electrodes were activated before every titration by soaking in 1 N permanganate solution containing 1 N sulphuric acid. Electrodes containing manganese dioxide were not pretreated.

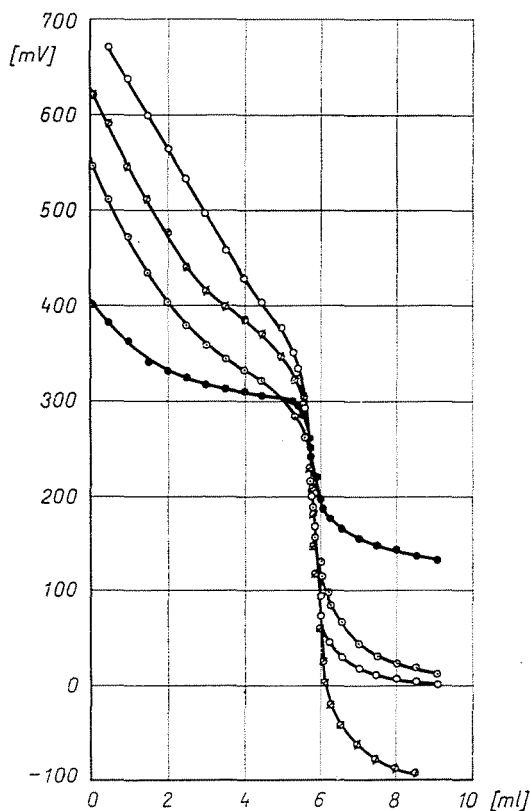


Fig. 2. Titration of 0.1169 N benzoic acid with 0.1008 N KOH in abs. methanol in the presence of different percentages (by volume) of dimethylformamide. Indicator electrode: graphite activated with N KMnO_4 — NH_2SO_4

Dimethylformamide content of the solution to be titrated: downwards 50, 70, 90, 100%

Figs 2 and 3 show the titration curves of benzoic acid with potassium hydroxide dissolved in abs. methanol, in the presence of different amounts of dimethylformamide and abs. methanol, resp. On the one hand activated graphite, on the other hand a graphite electrode containing 25% MnO_2 served as indicator electrodes.

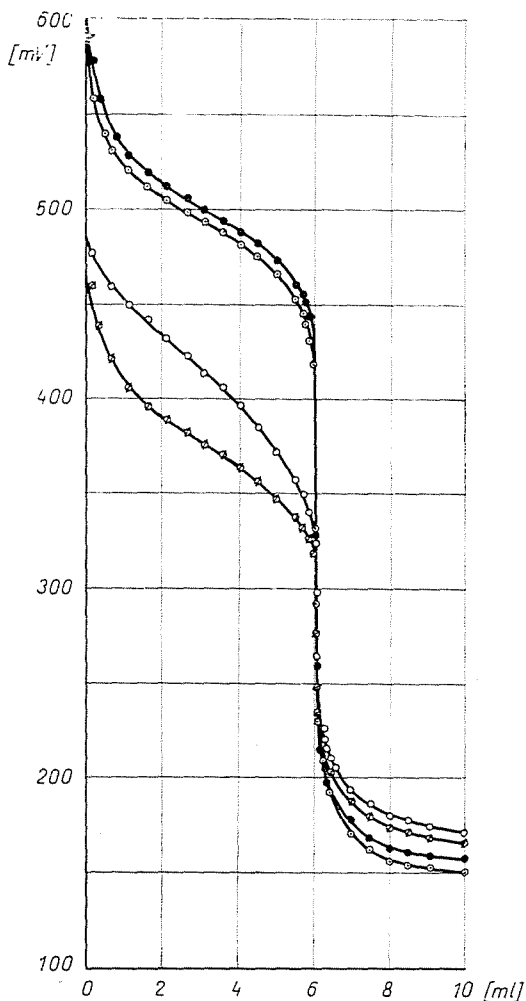


Fig. 3. Titration of 0.1209 N benzoic acid with 0.1008 N KOH dissolved in abs. methanol in the presence of different percentages (by volume) of methanol. Indicator electrode: Silicone rubber-based electrode containing 25% MnO_2 and 75% graphite. Methanol content of the solution to be titrated downwards 50, 70, 90, 100%

Discussion

The experimental results prove that silicone rubber-based graphite electrodes whether activated or non-activated, as well as silicone rubber-based electrodes containing manganese dioxide or the mixture of manganese dioxide and graphite are pH-sensitive, consequently they can be used as indicator electrodes to the end-point detection of potentiometric acid-base titrations.

The potential of the non-activated graphite electrode changes at an average of 30 mV per pH unit, while that of the activated graphite electrode

at 70 to 90 mV. For electrodes containing manganese dioxide and the mixture of manganese dioxide and graphite the electrode potential changes at 60 mV per pH unit.

The potential change of the activated electrode per pH unit is seen to be about 20 to 25% greater than that obtained with the glass electrode or any other conventional pH-sensitive electrode what is favourable for the titration of weak acids and bases.

The potential jump at the end-point of the titration was smaller when electrodes containing manganese dioxide in different amounts were used, than in the case of activated graphite electrodes. This potential jump, however though smaller, did not change even in the course of repeated titrations and due to the rapid potential reset, this type of electrodes could be applied to the end-point detection of automatic titrations too.

The electrodes described can be used in aqueous or non-aqueous solutions. Their mechanical resistance and the fact that — in contrast to glass electrodes — there is no need for pretreatment when used in non-aqueous solvents are further advantages of these electrodes.

Summary

Experiments were carried out with silicon rubber-based membrane electrodes consisting of graphite, manganese dioxide and the mixture of manganese dioxide and graphite, to establish whether they can be used as indicator electrodes to potentiometric titrations.

Authors found that the electrodes mentioned are pH-sensitive and can advantageously be used as indicator electrodes in acid-base titrations in both, aqueous and non-aqueous solutions.

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