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Effect of electrolyte composition on the properties of mercury electrochemical coulometers

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The results of studies on mercury capillary coulometers containing acidified electrolyte solutions (fluoroborate or perchlorate) or neutral solutions are presented. The effects of the solution composition on the coulometer properties such as internal resistance, current yield, and electrochemical stability are discussed. It has been shown that the solutions of mercury salts which contain fluoroboric or perchloric acid are more advantageous for use as mercury coulometer electrolytes than the iodide solutions used hitherto.

The mercury capillary coulometers which are discussed here are widely used as electrochemical integrators and as the working time meters of electrical instruments in laboratories and in industry.

1. Introduction

Mercury coulometers are a class of electrochemical instruments which have been employed since the nineteenth century.

They are mainly applied as working time meters in many electrical instruments, as electric charge meters, e.g. to control the battery capacity [1], and as integrators of slowly varying or pulse processes lasting hours, days, or even months. They are particularly useful in radiology and in climatology, e.g. for measurements of insolation, air temperature, wind force and direction, and so on.

The main advantages of mercury coulometers are: low size and weight; simple construction and ease of handling; and the ability to memorize the passed charge indefinitely with no external energy supply.

In recent years, simple modifications of mercury coulometers shaped as capillaries with mercury slugs spaced by an electrolyte solution layer containing mercury ions have been widely used for time and charge measurements. A current $i(t)$ flowing through such an element leads to mercury transport from one electrode to the other. The amount of transported mercury is related to the electric charge by Faraday's law:

$$m = \frac{E}{F}\int_0^t i(t)\,\mathrm{d}t \qquad (1)$$

where E denotes the chemical equivalent of mercury and F the Faraday constant.

According to [1], the electrical equivalent circuit of an electrocapillary coulometer consists of a capacitance and two resistances (Fig. 1) where the resistance R_1 denotes the resistance of the electrolyte solution while the resistance R_2 and the capacitance C_1 connected in parallel to each other represent the transport impedance of the ion which takes part in the electrode reaction through the solution.

As a rule, the authors of previously published works on mercury coulometers used solutions containing potassium iodide, in which mercury (II) ions were present as complex anions HgI_4^{2-} [2–6].

It is the aim of this work to present the results of studies on mercury coulometers which con-

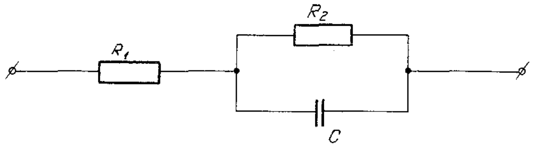

Fig. 1. Electrical equivalent circuit of mercury capillary coulometer.

tained acidified solutions prepared by adding fluoroboric or perchloric acid. In such solutions mercury (I) ions appear as diatomic Hg_2^{2+} cations [7, 8].

2. Experimental

2.1. *Preparation of mercury coulometers*

The coulometers have been prepared by filling glass capillaries with mercury and electrolyte solution by means of a syringe in such a way as to obtain two mercury columns separated by the solution. The capillary ends have then been sealed tight with an epoxy resin. Platinum wires protruded outside the mercury columns to serve as electric terminals. The salts to be used have been crystallized twice from triply distilled water and the acids have been analytical grade; analytical grade mercury has been distilled twice *in vacuo*.

2.2. *Measurement method*

The studies have been carried out under galvanostatic conditions by means of the apparatus shown in Fig. 2 which consisted of a constant current feeder (CF), a resistor (*R*) which determined the current value, a constant-current ammeter (mA), and a *Y–t* recording voltmeter (P).

The current yield of the electrode reaction is defined as the ratio of the quantity of mercury deposited on the cathode (or dissolved from the anode) to the charge, *q* which has passed through the coulometer. As both the mercury electrodes are placed in a capillary having a constant inner diameter, ϕ, the changes in electrode mass have been determined as column length variations, Δl (Fig. 3).

$$\Delta l = Kq \qquad (2)$$

where

$$K = \frac{4E}{\pi \rho F \phi^2} \qquad (3)$$

ρ denotes the density of mercury, and ϕ the inner diameter of the capillary which houses the mercury electrode. Because of the measurement method used, the current yield (K) is expressed in mm μC^{-1}. The Δl value has been measured with a microscope with a 0·05 mm accuracy.

The resistance and its components (R_1 and R_2) have been calculated from the voltage response of the coulometer to a current pulse longer than the time constant of the studied element (Fig. 4).

The measurements have been carried out at room temperature.

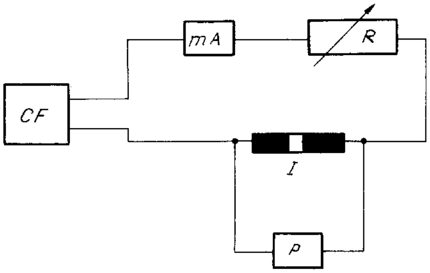

Fig. 2. Block diagram of the measuring apparatus.

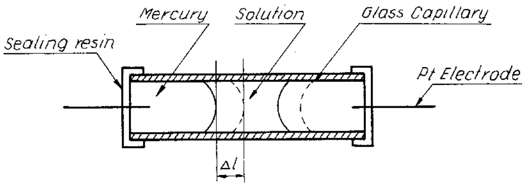

Fig. 3. Change in mercury electrode length caused by a flow of electric current.

3. Results and discussion

Experimental current yield values, K, as obtained from Relationship 2 are collected in Table 1 for the studied solutions at various current densities and charge passed values. Calculated current yield values obtained from Relationship 3 are presented in the K_ϕ column: the electrode process has been assumed to proceed according to the reaction:

$$Hg_2^{2+} + 2\,e \rightarrow 2\,Hg^o \qquad (4)$$

for acidified solutions and according to the reaction:

$$[HgI_4]^{2-} + 2\,e \rightarrow Hg^o + 4\,I^- \qquad (5)$$

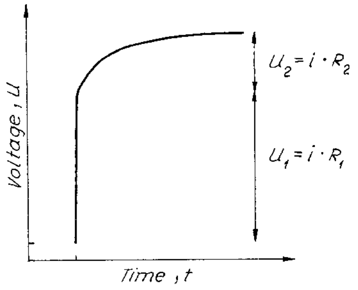

Fig. 4. Voltage response of a mercury coulometer to a current pulse.

Table 1. Calculated (K_ϕ) and experimental (K) current yield values

Number of integrator	*Electrolyte composition*		*j* (mA mm^{-2})	*q* (10^{-3} μC)	K_ϕ (mm μC^{-1})	*K* (mm μC^{-1})	$\frac{\lvert\Delta K\rvert}{K_\phi}$ (%)
7	2·2 N $HClO_4$	2·0 N $Hg_2(ClO_4)_2$	0·44	13·9	1·36	1·39	2·21
22			0·62	27·8	1·91	1·92	0·52
			1·33	55·6		1·93	1·05
			3·11	69·4		1·94	1·57
			6·22	69·4		1·92	0·52
11			4·41	277·8	1·36	1·36	0
1			5·35	347·2	1·64	1·64	0
25	5·0 N HBF_4	2·0 N $Hg_2(ClO_4)_2$	0·66	111·1	1·01	1·04	2·97
26			0·66	166·7		1·03	1·98
13	3·0 N HBF_4	2·0 N $Hg_2(ClO_4)_2$	0·44	13·9	1·36	1·37	0·74
			0·44	55·6		1·36	0
27			0·66	222·2	1·01	1·01	0
15	3·0 N HBF_4	1·0 N $Hg_2(ClO_4)_2$	0·44	55·6	1·36	1·33	2·21
			0·88	55·6		1·34	

Table 2. A comparison of the R_1 and R_2 values of the electrical equivalent circuit for the integrators containing iodide and perchlorate solutions

Number of integrator	*Electrolyte composition*		*j* (mA mm^{-2})	R_1 (Ω)	R_2 (Ω)
64	5 N KI	0·5 N HgI_2	0·11	168	240
			0·21	168	192
			0·42	152	192
			0·85	146	150
			2·12	138	106
			4·23	124	53
65	2·2 N $HClO_4$	2·0 N $Hg_2(ClO_4)_2$	0·11	156	100
			0·21	158	86
			0·42	157	73
			0·85	136	32
			2·12	136	26
			4·23	132	20

for neutral (iodide) solutions.

A comparison of the K_ϕ and K values shows that the assumed reactions proceed at practically 100% current efficiency in all solutions and over the entire current range. Small differences between K_ϕ and K values (about 3%) are within experimental error. The finding that the desired electrode reaction is the only one which occurs over the studied current range is illustrated by the plot of electrode length variation rate, $\Delta l/t$, versus the current density (Fig. 5). It is rectilinear and its slope is equal to the KS product where S denotes the electrode surface. Since S = constant for a given capillary, then the K value must also be constant and independent of current density. Rectilinear dependences have been obtained for all studied systems.

The results of studies on the resistances of mercury coulometers which contained various electrolytes are illustrated in Fig. 6. The coulometers containing iodide solutions are characterized by high resistances at low current densities. An analysis of the resistance components (Table 2) indicates that high transport resistance (R_2) values are attained by iodide solutions; at low current densities they are higher than the solution resistance, (R_1). This

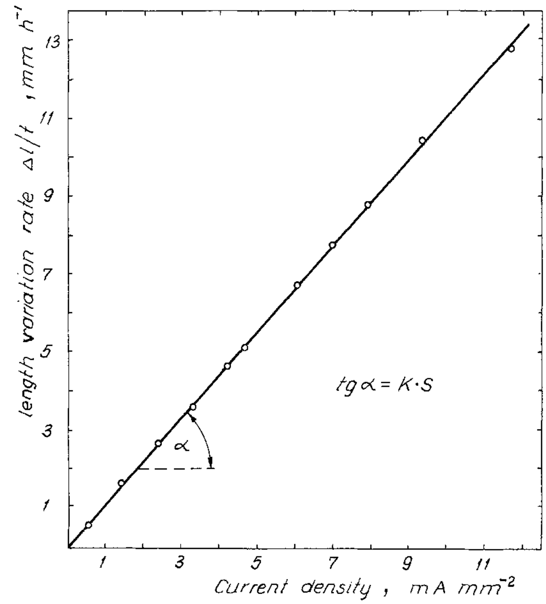

Fig. 5. Dependence of the length variation rate of the mercury electrode on current density.

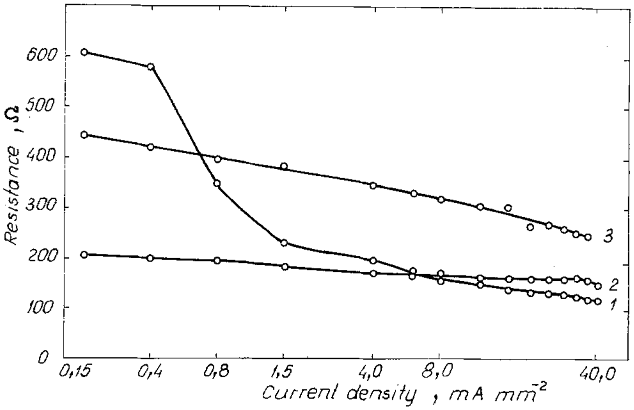

Fig. 6. Coulometer resistance as function of current density for the elements containing various electrolytes:
(1) 0·5 N HgI_2 + 5 N KI;
(2) 2·2 N $HClO_4$ + 2 N $Hg_2(ClO_4)_2$;
(3) 3·0 N HBF_4 + 2 N $Hg_2(ClO_4)_2$.

effect is probably due to the slowing down of the active ion (the negative complex) diffusion by the electric field; it does not appear for the acid solutions. This effect is evident at low current values where the contribution of diffusion resistance is important. Its role diminishes at higher current values due to an effective hydrodynamic mixing. The resistance is not so strongly current dependent for the acid solutions. In this case, the active ion, the cation, diffuses in the same direction as it migrates under the influence of the electric field.

4. Conclusions

The results presented here have indicated that the resistances of mercury–electrolyte solution–mercury systems are lower for mercury salt solutions containing fluoroboric or perchloric acid than for neutral, e.g. iodide, solutions. The current density dependence of the resistance is also lower for acidified solutions than for the neutral ones. These properties as well as the low freezing points of the HBF_4 and $HClO_4$ solutions which extend their working ranges down to − 60° C are particularly advantageous for applications of the Hg/electrolyte solution/Hg systems in coulometry, particularly for capillary microcoulometer. Standard potentials of Reactions 4 and 5 amounting to + 798 and − 40 mV, respectively, [9] also favour acidified mercury ion solutions over the neutral iodide solutions. The acidified solutions are more stable and undesired hydrogen ion reduction is less probable in their case.

It should be noted that fluoroborate solution have been applied in this work to the electrochemical study of mercury electrodes probably for the first time.

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