

A Photometric Coulometer

Masaki Nakanishi (中西正城)

Department of Chemistry, Faculty of Science,
Ochanomizu University, Tokyo

There have been several types of coulometers available for use in electrochemical works. Among them conventional silver coulometer, water coulometer and copper coulometer have long been used mostly for a rather large quantity of electricity, but they fail to insure the accuracy and precision required in an elaborate work involving less than several coulombs of electricity. Those coulometers that require titrations at the final step, despite the convenience to manage, depend on the accuracy and precision of the titration involved.

While several type of mechanical current integrators have been published, the coulometric coulometer by Ehlers and Sease¹⁾ seems to be reliable enough among chemical coulometers, except that a special equipment is needed as the trigger.

Franklin and Roth²⁾ previously reported a colorimetric coulometer, utilizing the change of an indicator color. The method, though it is suitable for precise measurement of a small quantity of electricity, contains the ambiguity of indefinite starting point and has a limited range as for the quantity of electricity. In this connection the present author has extended his earlier work of measuring ionic strength³⁾ to this type of coulometer.

In his preceding paper the author proposed an electrolytical method to measure the ionic strength of aqueous solutions, in which the linear relationship of the absorbance ratio of acid and alkaline absorption peaks of bromophenol blue vs. quantity of electricity was used. This offers a possible application to a coulometric use.

Theoretical Considerations

An apparent equilibrium for a weak indicator acid is given in its transformation interval as



therefore

$$\frac{(\text{I}^-)(\text{H}_3\text{O}^+)}{(\text{HI})} = K$$

or

$$\frac{(\text{HI})}{(\text{I}^-)} = \frac{(\text{H}_3\text{O}^+)}{K} \quad (2)$$

where HI and I⁻ represent the acid and alkaline forms, respectively, of the indicator acid, and the parentheses mean activities of the species concerned. These expressions are valid not only for monobasic indicator acid but also for dibasic, such as bromophenol blue.

The term on the left of Equation 2 can be rewritten as

$$\frac{(\text{HI})}{(\text{I}^-)} = \frac{f_0[\text{HI}]}{f[\text{I}^-]} = \frac{f_0 A}{f A_{Max}} \cdot \frac{A'_{Max}}{A'} \quad (3)$$

where

[] = concentration

f_0, f = activity coefficients of acid and alkaline forms, respectively, of the indicator

A_{Max}, A'_{Max} = absorbances of pure acid and alkaline forms, respectively, of the indicator at the wave length of their absorption peaks

A, A' = absorbances of the intermediate indicator form at the same wave length as A_{Max} and A'_{Max} , respectively.

Equations 2 and 3 are combined to give the following equation

$$\frac{A}{A'} = \frac{1}{K} \cdot \frac{f}{f_0} \cdot \frac{A_{Max}}{A'_{Max}} (\text{H}_3\text{O}^+) \quad (4)$$

If just enough strong acid is added to the solution to impart the acid color of the indicator and the solution is gradually neutralized with the cathodically generated base, the color of indicator changes through the intermediate into the alkaline range with the progress of electrolysis.

By differentiating Equation 4 with respect to quantity of electricity, q , which is consumed in electrolyzing the solution in question, the following expression is derived

$$\frac{d}{dq} \left\{ \frac{A}{A'} \right\} = \frac{1}{K} \cdot \frac{f}{f_0} \cdot \frac{A_{Max}}{A'_{Max}} \frac{d}{dq} (\text{H}_3\text{O}^+) \quad (5)$$

In case the solution is practically unbuffered and the current efficiency is maintained at 100% as for the neutralization reaction at the cathode, the term on the right of Equation 5 can be considered to remain constant throughout the electrolysis at a constant temperature. Thus, the ratio A/A' is interpreted to be a linear variable with respect to q in the transformation interval of the indicator.

Since f_0 and f are influenced by the ionic strength of the solu-

tion, the slope of the line representing the linearity differ with solutions of different ionic strengths. When a solution of a fixed composition is used, however, the quantity of electricity consumed can be estimated by measuring the change of the absorbance ratio A/A' . The equilibrium constant, K , is known to be practically indifferent to the slight change of the working temperature.

Apparatus

The electrolysis cell, which composed the essential part of the coulometer, consisted of a large weighing bottle of 60 ml. as illustrated.

in Fig. 1. A smooth platinum foil (7×10 mm.) was used as the generator cathode. The generator anode, a pure silver rod, was immersed in the 1*F* solution of sodium chloride as the anolyte. This was separated from the solution in the cathodic compartment by an agar containing sodium chloride. The solution in the cathodic compartment was stirred during the passage of electricity with a magnetic stirrer.

A constant voltage source at 200 v. maintained the constant current levels of about 1 or 9 ma. through a variable high resistance. A *pH* meter, manufactured by Mitamura Co., Tokyo,

was used to measure the exact current strength from the iR -drop through standard resistors of 1000 or 100 ohm. The quantity of electricity was calculated as product of a constant current and time, the latter being measured with a stop watch.

The Erma photoelectric colorimeter Model 5, manufactured by Matsunaga Co., Tokyo, equipped with interference filters, served for the absorbance measurements. The maximum transmittance of the filters were 45.0 and 26.4%, respectively, at their peaks at 439 and 594 $m\mu$ with half-width values of 11 and 7 $m\mu$ respectively.

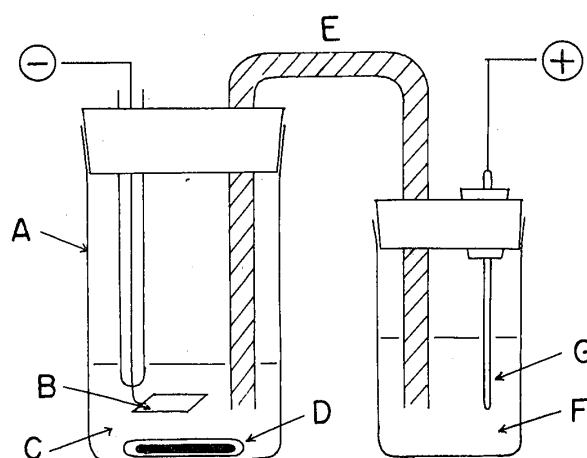


Fig. 1. Electrolysis Cell Assembly.

- A Electrolysis cell.
- B Pt Generator cathode
- C Electrolytic solution
- D Magnetic stirrer bar
- E NaCl bridge with agar
- F NaCl solution
- G Ag anode

Reagents

Guaranteed or extra-pure grade reagents of JIS (Japanese Industrial Standards) were used throughout the investigation.

About 2*F* stock solution of sodium chloride was prepared and standardized by potentiometric titration for chloride. It was diluted before use to the required concentration.

The indicator solution was prepared by dissolving 515 mg. of bromophenol blue in 100 ml. of distilled methanol, corresponding to 7.5×10^{-3} mole/l. The solution was kept in dark.

Hydrochloric acid was distilled in an all-glass apparatus and was diluted to 1.1*F*. It was standardized by coulometric argentometry.

The electrolytic solution for the catholyte was prepared by adding about 0.2 ml. of the indicator solution with a graduated pipet to 100 ml. of sodium chloride solution of various concentrations and it was acidified by adding hydrochloric acid solution in drops until the solution is tinged with the extreme acid-side color of the indicator in the transformation interval. The solution was usually prepared immediately before use, though it was useful after several days.

Results and Discussion

Bromophenol blue was used as the color indicator because of the merits described elsewhere.³⁾

It was ascertained again that the absorbance ratio, A/A' , holds linear plots against the quantity of electricity (Fig. 2), as was anticipated from the theoretical consideration.

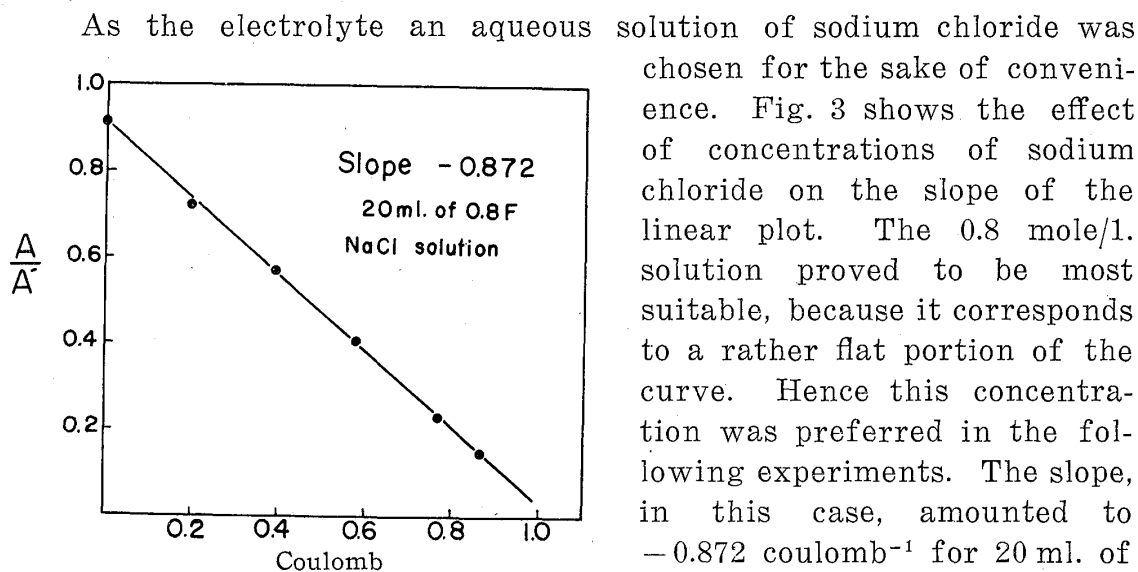


Fig. 2. Linear relation of absorbance ratio against quantity of electricity.

viously the slope became one n th of the value for 20 ml. of the solution. Thus, the larger the volume of electrolytic solution, the larger quantity of electricity was able to be measured.

For less than 2 coulomb of electricity it was sufficient for obtaining the accurate quantity to measure the absorbance ratios both before and after the electrolysis.

The recommended procedure goes as follows,

Pipet a suitable amount, say 20 ml., of the electrolytic solution into the electrolysis cell. Insert the platinum cathode through the salt bridge. Agitate for about one minute with a magnetic stirrer. Take a small portion of the solution into a cuvette and measure the absorbances at 439 and 594 $m\mu$ to obtain the initial absorbance ratio. Return back the solution as completely into the cell as possible. The electrolysis cell is then ready for the coulometric use. After the passage of electricity repeat to measure the absorbances at the same wave lengths to obtain the final absorbance ratio. The quantity of electricity passed is obtained by taking the difference of the final absorbance ratio from the initial and dividing it by the slope.

Table 1 summarizes the results from three typical runs, in which 20, 40 and 60 ml. of the electrolytic solution were used. The accuracy

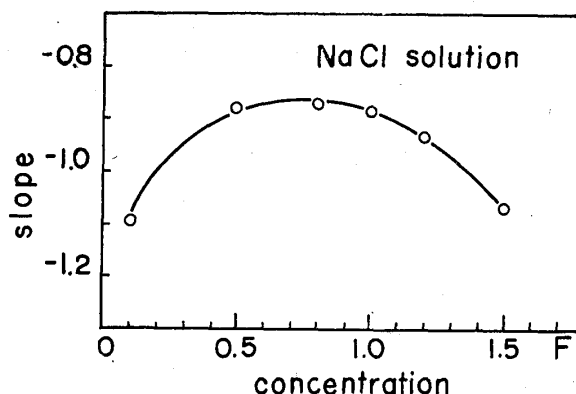


Fig. 3. Effect of concentration.

Table 1. Measurement of Smaller Quantity of Electricity.

Volume of solution (ml.)	Approximate current (ma.)	Absorbance ratio			Quantity of Electricity (coulomb)			
		Initial (A)	Final (B)	Slope (C) (coulomb)	Obs. $\left(\frac{A-B}{C}\right)$	Calc.	Error	
20	1	0.712	0.615	-0.872	0.111	0.107	0.004	
			0.436		0.316			0.319
			0.245		0.536			0.531
			0.073		0.733			0.742
40	9	0.637	0.477	-0.436	0.367	0.364	0.003	
			0.324		0.717			0.728
			0.163		1.087			1.088
60	9	0.682	0.577	-0.291	0.361	0.365	-0.004	
			0.313		1.268			1.278
			0.144		1.849			1.826

seems to be satisfactory.

In the present investigation not more than 60 ml. of the electrolytic solution was used. It will be probable, however, in principle that this kind of coulometer could afford to measure much quantity of electricity, if a sufficiently large cell might be applied, but the limited size of the apparatus prevented from trying it.

Alternatively another means was introduced for larger quantity of electricity. If the electrolysis continued beyond the allowance of the apparatus, the pH of the solution increased and the indicator assumed a completely alkaline color. An aliquot could be taken, after the electrolysis was over, from the solution of alkaline color, and be diluted with the original electrolytic solution so as to bring the pH in the transformation interval of the indicator. This essentially corresponded to using a larger volume of electrolytic solution, except that the volume was multiplied after, not before, the electrolysis.

Table 2. Measurement of Larger Quantity of Electricity.

Degree of dilution (Fold)	Quantity of Electricity (coulomb)		
	Obs.	Calc.	Error
2	1.035	1.057	-0.022
2	1.944	1.994	-0.050
3	2.188	2.109	0.079
4	5.449	5.623	-0.174
7	5.504	5.508	-0.004
9	9.919	10.225	-0.306

Several examples following this procedure are seen in Table 2. Negative errors, though not remarkable, predominate in the results. It is presumably due to a very slight buffering capacity of the original solution which was not revealed for smaller quantities of electricity, since this method depends for its validity on the current efficiency of 100 per cent with respect to the change of hydronium ion activity.

The author is indebted to Miss Itsuko Amano for her assistance in experiments.

Literature

- 1) V. B. Ehlers and J. W. Sease, *Anal. Chem.* 26, 513 (1954).
- 2) T. Franklin and C. C. Roth, *ibid.* 27, 1197 (1955).
- 3) M. Nakanishi, *ibid.* 30, 1988 (1958).