THE MILLICOULOMETRIC METHOD FOR n-VALUES

by

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INTRODUCTION

The technique of measuring the total current during electrolysis of a small amount of solution with a dropping mercury electrode has been used to determine the number of electrons involved in polarographic reduction processes. This technique has been called "Millicoulometry". Although millicoulometry should be ideally suited for the determination of the number of electrons involved in the reduction of irreversible systems at the dropping mercury electrode, it has been the experience of the authors and others working in this field[1-9] that many variables must be carefully controlled and unknown sources of error disclosed before reliable information can be obtained as in macrocoulometry[10,11,12]. It is the purpose of this study to discuss, in general, the method of determining n-values by millicoulometry, its advantages and disadvantages, the sources of error, an application of the method to the nitro-nitrosoguanidine system, and in conclusion propose some recommendations for future work.

PRINCIPLES

Millicoulometry involves, essentially, the measurement (direct or indirect) of the total current passed during the polarographic reduction of a compound at constant potential, the measurement of the amount of compound reduced by this current, and finally the calculation of n (the number of electrons per molecule involved in electrolysis) by application of Faraday's laws.

The expression of Faraday's law used in the calculation of n-values is:

$$n = \frac{c}{F\,m}$$

where c is the number of coulombs passed during the reduction, m is the number of moles of the depolarizer reduced by the passage of c, and F is the Faraday or 96,500 coulombs. Thus, one need only know the amount of electricity consumed and the amount of compound reduced by that quantity of electricity to directly determine an n-value.

Since very small currents are used in millicoulometry, one must work with small volumes of solution to affect a concentration change of reasonable magnitude. For example, using a volume of 0.3 ml of solution, a concentration change of 50% may be obtained in a 2-h electrolysis. The concentration change is usually determined by running a polarogram immediately preceding the start of the run and then again at the end of the run. If the step-height of the compound is proportional to concentration,

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then the equation for the number of moles reduced during an electrolysis may be given by:

$$m = \left(1 - \frac{H_2}{H_1}\right)KC$$

In this equation H_1 and H_2 are the step-heights before and after electrolysis, respectively (Fig. 1), K is the volume (ml) of solution, and C is the concentration (moles/ml) of the depolarizer in solution.

The determination of the number of coulombs passed is made by integration of the area under the current – time record[1]. The integration may be accomplished with electromechanical integrators[6], or by simply weighing the paper of the area under a chart-recorded polarogram or calculating the area with a planimeter. The use of electromechanical integrators would seem to be preferred for precision and simplicity.

ADVANTAGES AND DISADVANTAGES

The main advantage of the millicoulometric method lies in the fact that it is a direct and rapid technique for determining n-values under the same conditions as one operates in polarography; thus, the reduction occurs at the dropping mercury electrode. In the case of rate-controlled reactions, as so many organic reductions may be, the n-values obtained by macrocoulometry and millicoulometry may be different because the final reduction products at a well-stirred large cathode may not be identical to those obtained by electrolysis at the dropping mercury electrode[13]. In addition, millicoulometry appears to be a useful technique for determining n-values of compounds that hydrolyze or decompose rapidly. For example, in work on nitrosoguanidine, it was found that this compound hydrolyzed too rapidly to obtain a reliable diffusion coefficient experimentally. The equipment needed in millicoulometry is usually easy to assemble and the desired applied potential for the electrolysis may be supplied by a polarograph.

When electrolysis at the dropping mercury electrode is carried out long enough to effect a change in concentration of the depolarizer of reasonable magnitude, there is always the danger of the reduction products further reducing, oxidizing at the anode, or reacting with one another. However, there should be less danger of this in millicoulometry than in macrocoulometry if one carries out the electrolysis only long enough to give a measurable change in the concentration of original reducible material. Another possible disadvantage of millicoulometry may be its value with reversible systems. However, if one uses a divided cell, both reversible systems and complex electrode processes might be conveniently and precisely studied.

SOURCES OF ERROR

During electrolysis of such small volumes of solution as are employed in millicoulometry, the concentration of depolarizer surrounding the mercury drop may be less than that of the main body of the solution. Thus, at no time during an electrolysis may the current flow be assumed to be proportional to the concentration of the solution. This necessitates a thorough stirring of the solution before the concentration of depolarizer is determined. This tendency of the solution to be less concentrated at the drop

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compared to the main body of solution has been termed the "depletion effect" and has been cited as a source of error in millicoulometry[6]. However, with the integration technique of REYNOLDS AND SHALGOSKY[1], if concentration is determined only after adequate stirring, no error due to this cause should exist.

It is necessary that only the current that reduces the depolarizer be employed in the calculation of n-values. Thus, the current flow due to charging current and the reduction of trace impurities must be subtracted from the total current flow. This residual current may be considered as that current giving rise to the open deflections from the zero current line at 10 mm to 12 mm at point A in Fig. 1. The line at 12 mm may then be considered as the base from which concentration and current will be measured. The level of this residual current should be constant during an electrolysis.

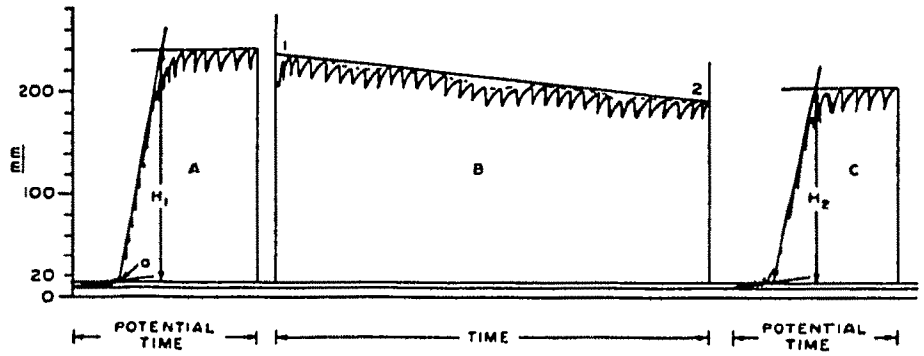

Fig. 1 Section of typical n-run.

A valid n-value for a particular compound may be obtained only if the reactions giving rise to its wave do not change during an n-run. Such changes in electrode reactions, due, possibly, to the increasing concentration of reduced species, may be detected by plotting the number of moles reduced at any time during the run against the number of coulombs passed during the same interval. Such a plot should yield a straight line passing through the origin and having a slope of $(nF)^{-1}$. If such a plot yields a curved line, a changing electrode process may be suspected. If the plot does not pass through the origin, constant errors in current calibration or concentration measurement may be responsible.

Sources of error in millicoulometry may be due to:

(1) Oxidation of a reduced species at the anode. This may be prevented by use of a divided cell, or use of an undivided cell using an anode other than the mercury pool.

(2) Electrolyzing over too long a period. This is especially important if the reduced species may undergo further slow reduction or react with the initial substance. In addition, the primary product might undergo some non-electrolytic transformation (as hydrolysis).

(3) Selection of an incorrect electrolysis potential. One should electrolyze on the limiting value of the diffusion current in order to obtain data pertaining to the entire process.

(4) Failure to meet usual polarographic requirements. Adequately buffered solutions should be employed and oxygen contamination must be removed and prevented.

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(5) Use of mercury pool anode. Resolution of amalgam formed at dropping mercury electrode during electrolysis occurs more easily with this anode. The use of a separate anode (silver) affords good results. In addition, the choice of anode must be such that the reduction products or primary product can not react with the electrode.

EXPERIMENTAL

The apparatus used in this study for the determination of the n-values of p-nitroaniline, nitrosoguanidine, and nitroguanidine was a modification of the design used by REYNOLDS AND SHALGOSKY (Fig. 2). The assembly consisted of four principal parts. The beaker serves as a mercury reservoir to maintain constant mercury height within the microcell. The microcell, which is supported by a closely fitting plastic ring, serves as the actual cell and envelope to exclude oxygen. The microcell stopper is made by drilling holes in a frozen No. 11 solid-rubber stopper. This assures sliding fits of the various components. The stopper contains a flushing tube capillary, a capillary shoe (a device to eliminate vibration of the dropping mercury electrode), and a nitrogen inlet tube through which nitrogen is constantly passed during an n-run. The nitrogen used was obtained from compressed gas cylinders. Traces of oxygen present in the nitrogen were removed by passing the gas over copper turnings heated to 450°C. These traces of oxygen were removed whenever dilute solutions requiring high polarographic sensitivities were run. The cell and nitrogen atmosphere arrangement was such that no increase in residual current due to oxygen absorption occurred even after standing for 3 h. The flushing tube is drawn from 6-mm tubing and the right-angle bends

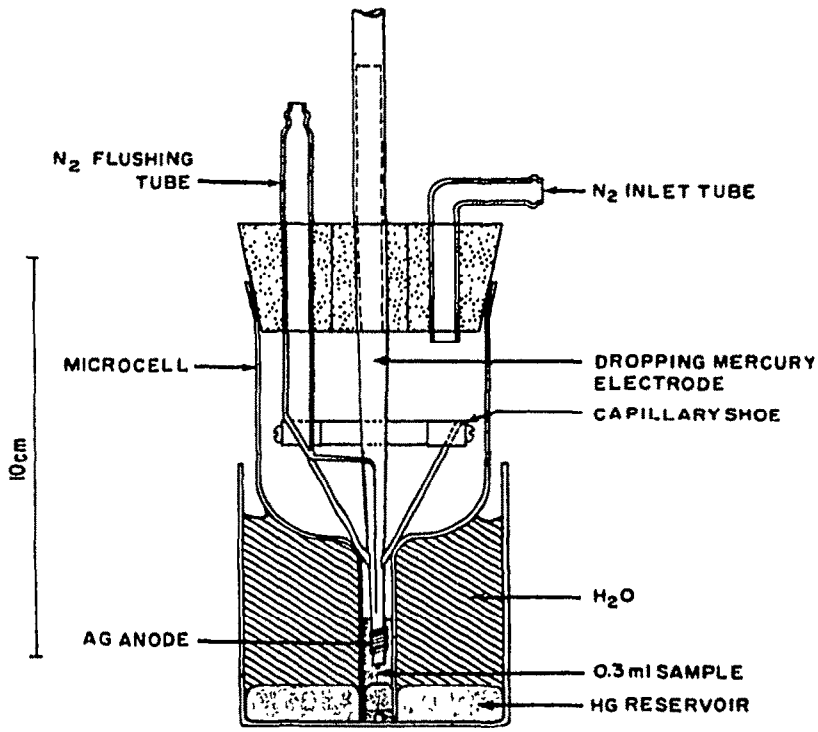

Fig. 2. Microcell assembly.

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are made by heating the capillary with a very small flame and allowing the weight of the capillary to form the bend. The pressure for the flushing tube is achieved by a conventional variable water-height pressure regulator. Excess nitrogen is passed through the nitrogen inlet tube. The dropping mercury electrode is fabricated from commercial capillary tubing by tapering the tubing to an end diameter of 2 mm on a wet-belt sander. The electrode surface is polished in a lathe with carborundum powder of 150-500 grit. Four capillaries can easily be prepared in 2 h using this method. The authors' experience has indicated that capillaries prepared by this method are mechanically stronger and more likely to have constant drop rates than those prepared by drawing out marine barometer tubing in a flame. The silver anode is prepared from pure silver wire (0.020 in. in diameter) by winding into helical form to fit the capillary. A mandrel, shaped to the dimensions of the capillary, is used to form the anode. The windings are close and consist of a convenient number of turns (the authors used eight turns). Anodes prepared in this manner are almost identical. The anode is placed on the capillary to a height of 3 mm from the tip, and the end soldered to the copper wire winding on the capillary that leads to the polarograph anode terminal. The same capillary, stopper, and cell arrangement have been incorporated in a divided cell (Fig. 3). This divided cell is similar to that of MEITES[10].

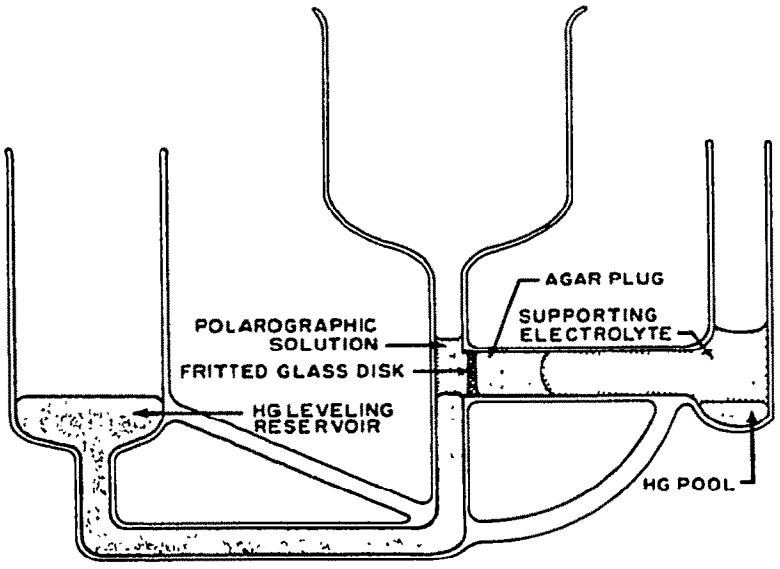

Fig. 3 Divided microcell assembly.

When one is working with irreversible systems, the supporting electrolyte should be well buffered. The successful use of a silver anode depends upon the formation of an insoluble silver salt during reduction. For this reason, KCl was present in all buffer solutions. Solvent systems that will form complexes or in any way affect the solvation of silver should not be used[16]. The position of the silver anode from the tip of the capillary did not appear to be critical. Anodes were changed frequently because they became amalgamated quite easily. The effect of amalgamation upon the polaro-

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graphic waves was not determined, but every effort was made to prevent use of an amalgamated anode.

The relationship between step-height and concentration was established in a polarographic cell using 10 ml of solution. After these calibration data were obtained, the beaker containing mercury was placed in a constant temperature bath at 30°C, the microcell was placed therein, and 0.30 ml of solution was then introduced by means of a graduated pipette. The apparatus was further assembled (Fig. 2) and the solution was flushed for 10 min. A polarogram was then obtained. The potential applied to the cell was held constant at a value lying on the more positive portion of the diffusion plateau. Between the running of the polarogram and the constant potential run, the chart was turned ahead by hand to allow space for calculation. During this time the dropping mercury electrode (DME) was removed from the circuit by means of the switch provided in the instrument. After setting the instrument to the desired potential, the DME switch and the chart motor were turned on simultaneously. When reduction had proceeded for 1/2 h, the chart motor and the DME switch were turned off simultaneously. The solution was again flushed for 5 min and a polarogram obtained. Since the voltage axis of the polarogram is also a time axis, integration of these polarograms may be carried out in the same manner as was employed with the constant voltage section (Fig. 1).

An alternate method, which may be used to advantage in the case of compounds producing only a single wave, is that of not running an initial and final polarogram, but taking the current at constant potential immediately after flushing as being proportional to concentration. This method simplifies the calculations considerably.

The undivided microcell and silver anode were employed in all work. The drop rate of the capillary was approximately 5 sec/drop at —1.2 V (applied to cell) in pH 10 Clark and Lubs' buffer[17] (2 ×).

RESULTS AND DISCUSSION

p-*Nitroaniline*

The standard chosen to test the method was *p*-nitroaniline (PNA). This compound requires 6 electrons per molecule for reduction and was investigated by REYNOLDS AND SHALGOSKY, who employed 0.1 *N* KCl as the supporting electrolyte. The guanidine compounds under consideration had previously been studied polarographically at pH 10 in a Clark and Lubs' buffer. This system was chosen for PNA so that a direct comparison of *n*-values could be made. The PNA was crystallized three times from water and melted through the range 146.0-146.5°C.

The buffer solutions were prepared from reagent grade chemicals. Table I lists the *n*-values obtained with *p*-nitroaniline using the integration method and the 6/7 peak current method[14]. Each of the *n*-runs was for 1/2 h. These data were obtained at a residual current potential of —0.6 V applied to the cell and —1.2 V at the diffusion current plateau.

The range of results for each section is greater than the range in *n*-values between runs because the method depends upon the measurement of a difference in concentrations. Thus, if the initial concentration in Fig. 1 is such that H_1 is 200 mm, which was usually the case, then the step-height after the first 1/2-h section of reduction (H_2) would be approximately 200—(1/4 × 50% × 200) or 175 assuming a 50% reduction after

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TABLE I

n-VALUE RESULTS OF p-NITROANILINE, PH 10

$c \cdot 10^3$	$m \cdot 10^7$	n-Values obtained per section					vol. used (ml)
		1	2	3	4	n	
1 430	2.471	6 32	5.78	6 14	5.57	6 00[a]	0 30
1.648	2.789	6.35	5 87	6 28	5.94	6 12[a]	0.45
0 8465	1.382	6.31	5.95	6.36	6.97	6 34[b]	0.45
0.6740	1.223	5.28	5 97	5.89	5 79	5.71[b]	0.30

[a] 1.6 mM
[b] 0.8 mM

four 1/2-h sections. This difference of 25 mm, corresponding to the reduction in concentration during the first section, is subject to a 2% error in the 200- and 175-mm step-heights. Thus, an error of as much as 8 mm may be incorporated in this difference which is more than 30% error for that section. For this reason, it is best to carry out a number of sections of reduction.

The residual current for these data was measured at —0.6 V applied to the cell and was initially about 13 mm in height (the zero-current position was 10 mm). An increase in this residual current was observed after each section of reduction in all the n-runs with PNA at pH 10.0. This increase in residual current did not occur in equal increments, but increased rapidly to a constant value. Thus, at the beginning of the third section, the residual current was usually 22 mm; but at the end of the fourth section it had increased to only 25 mm. Attempts to discover the cause of this increase in residual current were unsuccessful. No such increase has been noted during the identical treatment of the buffer solution alone, indicating that this increase is directly related to the reduction of the PNA. This conclusion is supported further by the fact that reductions with nitro and nitrosoguanidine in this system showed no increase in residual current.

Nitroguanidine

From study of the data obtained with p-nitroaniline it was decided that the millicoulometric method as employed here should provide satisfactory data with the nitro-nitrosoguanidine system. Therefore, nitroguanidine was investigated in a Clark and Lubs' buffer of pH 10. Polarographically, nitroguanidine produces a single, well-defined wave at this pH. Table II presents the n-values obtained. The residual current was measured at —0.86 V applied to the cell and the diffusion current at —1.58 V.

TABLE II

n-VALUES OF NITROGUANIDINE, PH 10.0

Initial conc. (mM)	$c \cdot 10^3$	$m \cdot 10^7$	n-Values obtained per section				
			1	2	3	4	n
1.36	8.154	1 951	4.31	4.91	5.23	4.88	4.76
1.24	6 675	1.496	4.84	5.52	5.29	—	5.08
1.44	7.303	1 561	5.24	5.11	6.29	4.92	5.33
2.40	18.91	3.855	5.20	4.87	5.07	5 23	5 09
2.40	15.07	3.123	4.63	5.32	5.19	—	5.00

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Samples of 0.3 ml were used in all runs. The data indicate that nitroguanidine reduces by means of a 5-electron-per-molecule reduction process at the dropping mercury electrode in this pH 10 medium. Thus, the reduction of nitroguanidine in this case does not appear to be a simple process, but may be explained by a coupling of the products of a 2- and 6-electron reduction (Fig. 4). Since nitroguanidine has been investigated and found to reduce directly to aminoguanidine in acid solution[18], a 2.5-mM solution of the compound was studied in 6N HCl. An average n-value of 6.35 was obtained in this medium.

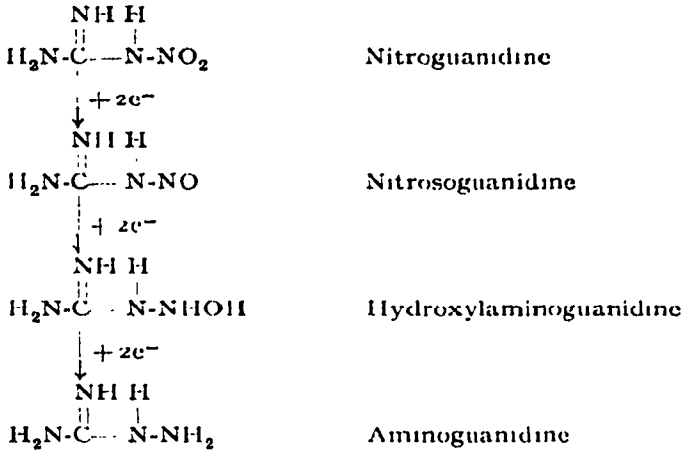

Fig. 4. Possible reduction mechanism for the nitro-nitrosoguanidine system.

Nitrosoguanidine

An investigation of this compound was also made in a Clark and Lubs' buffer of pH 10. The oxidation state of nitrosoguanidine differs from that of nitroguanidine by 2 electrons per molecule (Fig. 4). Thus, the n-value of nitrosoguanidine would be expected to be 2 electrons per molecule less than that of nitroguanidine, if the reduction process of nitroguanidine passed through nitrosoguanidine. This was shown to be the case. The results are shown in Table III. Considered separately, the value of 3 electrons per molecule of nitrosoguanidine is as difficult to interpret as the 5 electron value for nitroguanidine. However, the difference of 2 electrons between the reductions appears to indicate that the reduction of nitroguanidine to nitrosoguanidine is a fairly straightforward process, and that the odd numbered electron changes are the result of somewhat complex processes occurring beyond the nitroso state.

TABLE III

n-VALUE OF NITROSOGUANIDINE AT pH 10

Initial conc. (mM)	% *Reduction*	$c \cdot 10^3$	$m \cdot 10^7$	n
4.0	35.3	10.922	4 270	2.89
4.0	41.9	13.604	5.041	3.06
4 0	47 8	15.898	5.738	3.13
4 0	49.9	15.749	6 034	2.96
0.4	54 5	1 920	0.656	3.31

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CONCLUSIONS

Although the millicoulometric method appears, and has been shown by some workers in the field, to give reliable data for n-values, it is the conclusion of the authors that many known variables must be carefully controlled and some hidden factors yet disclosed before this method can be trusted implicitly. Since this method appears to be ideally suited for irreversible reductions and for studying reactions at the dropping mercury electrode, it would be a great aid to those working in the field if further research could confirm its potentiality. With this in mind, the following recommendations for future work in millicoulometry are proposed.

(1) Methods of coulomb measurement should be critically examined with acceptable standards and applied to millicoulometric studies.

(2) Methods of concentration measurement not dependent upon the polarograph should be investigated.

(3) Apparatus should be designed and evaluated as to reliability for n-values.

(4) Similar millicoulometric studies of organic compounds should be made. Effect of pH, concentration, and supporting electrolyte should be critically examined.

(5) Compare reactions (n-values) occurring at a large mercury electrode with those at a dropping mercury electrode.

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SUMMARY

Millicoulometry as applied to the determination of n-values has been discussed in general with emphasis on its advantages and disadvantages, the main sources of error, and an application of the method to the nitro-nitrosoguanidine system. Results are discussed and recommendations for future work in the field are proposed.

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