THE COMPUTERIZED DETERMINATION OF DOUBLE-LAYER CAPACITANCE WITH THE USE OF KALOUSEK-TYPE WAVEFORMS AND ITS APPLICATION IN TITRIMETRY

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SUMMARY

A method for the rapid determination of double-layer capacitance—potential curves of electrodes is described. An on-line computer is used to apply Kalousek-type waveforms to the electrochemical cell and to measure the accompanying current response. The capacitances are determined from the slope of the plots of log current against time. For 0.1 M KCl, the computerized method agrees well with the bridge method, except for the potential range of 0 to —0.15 V. The method is very useful for automating titrations with tensammetric detection of the end-point. The method is applied to the titration of barium with a macrocyclic compound (kryptofix 222) and the titration of cetyl-trimethyl-ammonium bromide with bromocresol purple. The accuracy of the titrations is ±2%.

Differential capacitance—potential curves of electrodes play an important role in studies of the electrical double layer. Tensammetry is the electro-analytical technique based on the measurement of these curves [1]. Its use has not been widespread, mainly because of the complex relationship between capacitance and concentration of the compounds of interest and also because of the complex equipment required for the measurements. If the technique is used to determine titration end-points, quantitative results can be obtained from the stoichiometry of the titration reaction [2] and the first drawback can thus be circumvented. The computerization of the method described here is meant to simplify the measurements to such an extent that routine application will be possible.

Various methods have been described for the determination of the capacitance of the electrical double layer [3—6]. The impedance bridge method is still believed to be the most accurate one, but it is very time-consuming. All other methods described so far rely on measurements on an oscilloscope screen, which are also rather tedious. Phase-selective tensammetry [7] is an exception in that aspect as there are direct-recording instruments for this technique. However, its use for end-point detection in titrations still requires many manual operations.

This paper describes a computer technique for the determination of the

capacitance of the electrical double layer and its use in computer-controlled titrations.

THEORY

Capacitance measurements

In the absence of faradaic currents, the electrical equivalent of an electrochemical cell consists of a capacitor C and a resistor R connected in series.

If a voltage step of magnitude ΔV is applied to the cell, its current response, from charging of the capacitor, will be

$$i_c = (\Delta V/R) \exp (-t/RC) \tag{1}$$

For a periodic square-wave signal with a period much greater than RC, the current response is given in Fig. 1. At the end of both half-periods, the current has dropped to zero and the voltage across the capacitor has reached the applied voltage, either V_t or V_b. Equation (1) can be plotted logarithmically to give a straight line:

$$\ln i_c = \ln (\Delta V/R) - (t/RC) \tag{2}$$

The slope of this plot is $-(RC)^{-1}$. To be able to determine the double-layer capacitance at a known predetermined value of the d.c. potential V_t of the dropping mercury electrode (DME) the following conditions should be fulfilled: $t \ll RC$ and $T/2 \gg RC$. This means that the current can be measured only during a short interval after the reversals, whereas the frequency of the square wave should be limited to low values. Actual values for these limits will depend on the series resistance and the capacitance of the circuit. For accurate determination of the double-layer capacitance, the current measure-
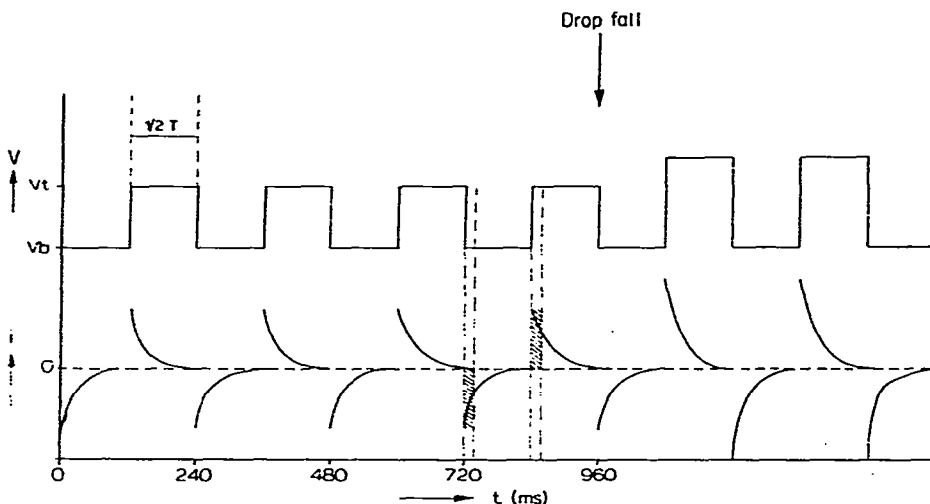

Fig. 1. Applied voltage and current—time patterns in the absence of faradaic currents.

meants should be performed after a reversal near the end of the drop life where the relative change of its surface can be neglected.

In the absence of faradaic currents, one pulse and current measurements directly after the flank of the pulse will suffice to determine the double-layer capacitance. The application of Kalousek-type waveforms offers no special facilities in this case. However, in the presence of electroactive species, capacitance changes at V_b (Fig. 1) should be observed if tensammetrically active substances are being produced during the V_t half-period. For reversible electrode reactions, pseudo-capacitance peaks will be observed in the $C(V_b)$—V_t curves. These can be distinguished from the tensammetric processes by observation of the corresponding Kalousek polarograms: type II polarograms show a wave in the same region.

Titrations with tensammetric end-point detection

Tensammetry has been used for end-point detection in various types of titrations [2, 8]. This type of end-point detection requires that the titration reaction produces or liberates a tensammetric compound or that it consumes such a compound. A distinction should be made between the two different ways of assessing the concentration of a compound tensammetrically, i.e. (a) by measuring the height of the adsorption/desorption peaks and (b) by measuring the lowering of the double-layer capacitance in the potential region of maximum adsorption. Normally method (a) is more sensitive and more selective, but sometimes a compound that is tensammetrically active does not show adsorption/desorption peaks. Then measurement of the lowering of the capacitance of the double layer becomes necessary.

Generally, the adsorption isotherms show a straight line at low concentrations [9]. This gives titration plots from which the end-point can be found as the intersection of two linear parts for titrations of a tensammetrically active substance and for titrations with a tensammetrically active titrant.

EXPERIMENTAL

Chemicals

Potassium chloride (Merck, zur Analyse), mercury (Drijfhout, polarographic grade), alizarin complexone dihydrate (Aldrich), cetyltrimethylammonium bromide (Merck, zur Analyse) and bromocresol purple (Merck, indicator grade) were used as received. Throughout the experiments, deionized water which was also filtered through Millipore Q2 filters was used.

Equipment

A diagram of the equipment is shown in Fig. 2. A Radiometer polarographic stand (type E64) equipped with a drop-life timer (type DLT1) was used. The dropping mercury electrode had the following characteristics: $h = 52$ cm, $m = 2.58$ mg s^{-1}, $t = 3.25$ s (1 M KCl, open circuit). Computer control of the Mettler motor burette (type DV11) was established by connecting its trigger terminals to the D/A converter of the computer.
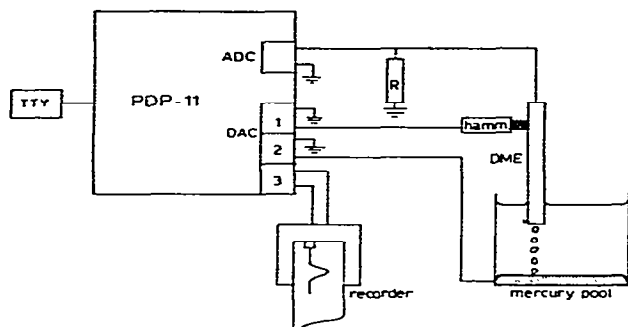
Fig. 2. Equipment for computerized titrations with tensammetric end-point detection.

Procedures

All solutions were freed from oxygen by bubbling with nitrogen for 10 min. During the titrations, the titrant stream and the contents of the cell were mixed by means of the nitrogen stream, except for the titrations of cetyltrimethylammonium bromide where magnetic stirring was used. The time between two successive titrant additions was at least 10 s, to allow for mixing of the titrant. The end-points of the titrations were found by calculating the intersection point of two least-square lines in the titration plots.

COMPUTER PROGRAMS

The program for acquiring the current—time data was the same as used in the KALOUSEK program [10], with the number of pulses per drop-life time restricted to 4. For automatic recording of double-layer capacitance as a function of potential, the data stored by this program on disc were used by a second program that calculated the capacitance values by a least-squares fit of the data to eqn. (2). To fulfil the conditions mentioned for t and $T/2$, only the values of the current up to 4 ms after the reversals of the last period were used in the calculations (shaded area in Fig. 1). The current was sampled at a rate of about 3 kC, so that 12 points were available. The program outputs the results either in tabular form or on a strip-chart recorder. The double-layer capacitance at the pulse base potential and the value at the pulse top potential were plotted.

The operator has control over the following experimental parameters: drop time, pulse base potential and the values that determine the scan of the pulse top potential, i.e. starting value, scan rate and end value.

The program for the automatic titrations with tensammetric detection of the end-point used the same routines for data acquisition and calculations, but was extended by routines for controlling the burette and for averaging the capacitance values obtained for several successive mercury drops. It operated with a fixed pulse base and pulse top potential. The experimental parameters that can be adjusted by the operator are pulse base potential,

TABLE 1

Calibration of equipment with standard capacitors

Capacitance (μF)	Computer result			Mean
0.05	14.56	14.44	14.55	14.51
0.10	29.41	29.64	29.39	29.48
0.15	45.56	45.54	45.56	45.55
0.25	76.31	75.15	74.33	75.39
0.50	143.7	142.9	143.3	143.3
0.75	212.4	213.5	213.9	213.9
1.00	287.2	291.1	281.6	286.6

pulse top potential, drop time, number of mercury drops for which the capacitance values are to be averaged per titration step, titrant volume increment per titration step, and the total volume of titrant to be added during the titration.

RESULTS AND DISCUSSION

Calibration

To calibrate the method, the polarographic cell was replaced by a standard capacitor decade. For a number of known capacitance values the computer result for the slope of the plot of log i against t was obtained with a measuring resistor of 1 MΩ, a pulse base potential of 0 V and a pulse top potential of +1.0 V. The data are given in Table 1. The result can be expressed as capacitance (μF) = (computer result −1.824)/284.2. The value of the intercept (1.824) can be explained by the capacitance of the cable used for the computer connections.

Double-layer capacitance measurements for 0.1 M KCl

For potassium chloride, accurate values are available for the double-layer capacitance at the mercury electrode obtained by the bridge method [11]. These were used to check the computerized method. The comparison is given in Fig. 3. In the computerized measurements, a drop time of 960 ms, a measuring resistor of 1 MΩ and a pulse base potential of −1.6V were used. As can be seen, there is fair agreement except for the potential range of 0 to −0.15 V. No explanation can so far be offered for the discrepancies in this region.

Titration of barium with cryptand 2.2.2

Cryptand 2.2.2 reacts with barium ions to form a 1:1 BaL complex. The formation constant, $K = [LBa^{2+}]/[L][Ba^{2+}]$, has the value of $10^{9.5}$ as determined by Lehn and Sauvage [12]. Therefore, this reaction can be used for the titration of barium ions if a suitable method of end-point indication can
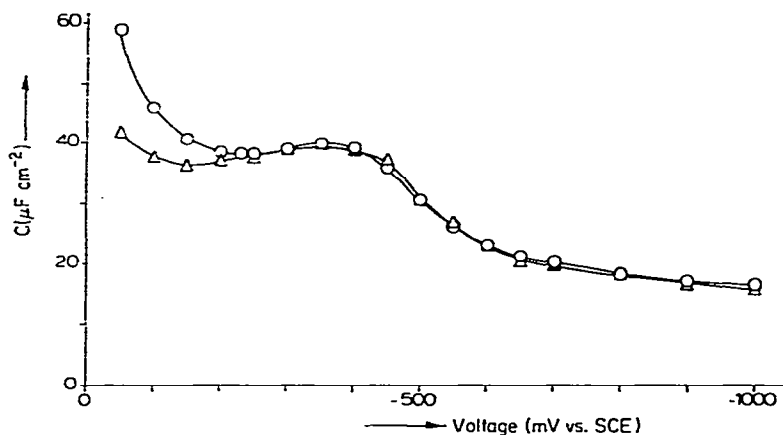
Fig. 3. Differential capacitance data for 0.1 M KCl (o) Grahame [11]; (△) this work.
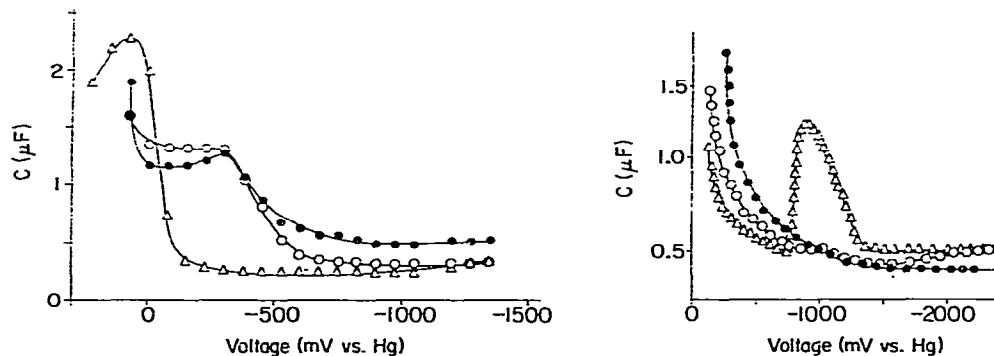

Fig. 4. Differential capacitances in 0.1 M LiCl for (●) 2 × 10^{-4} M Ba^{2+}, (△) 1.4 × 10^{-3} M cryptand 2.2.2, and (o) 2.4 × 10^{-4} M Ba—cryptand 2.2.2 complex.

Fig. 5. Differential capacitances in acetate buffer pH 4.62 for (△) bromocresol purple, (●) CTAB, and (o) bromocresol purple—CTAB complex.

be found. Tensammetric activity has been found [13] for some cryptand complexes. Therefore, it was expected that tensammetry could provide a means of end-point detection of this titration. Figure 4 shows the tensammograms of uncomplexed barium ions, the free cryptand 2.2.2 and a mixture of 1:1 barium and cryptand 2.2.2. The measurements were carried out in 0.1 M LiCl with a pulse base potential of −1.5 V at concentrations of 2.4 × 10^{-4}, 1.4 × 10^{-3} and 2.4 × 10^{-4} M. It can be seen that the presence of uncomplexed cryptand 2.2.2 can be detected from the capacitance values between −0.1 and −0.4 V. With a measuring potential of −0.4 V and a pulse base potential of −1.5 V, the double-layer capacitances were determined during titrations of various amounts of barium ions with 0.0100 M cryptand 2.2.2. Table 2 shows the results of the titrations.

TABLE 2

Tensammetric titration of barium with cryptand 2.2.2 in a 0.1 M LiCl medium

Barium taken (mg)	Barium found (mg)	Error (%)	Barium taken (mg)	Barium found (mg)	Error (%)
0.711	0.738	+3.8	1.401	1.408	+0.5
1.356	1.373	+1.3	1.684	1.717	+2.0
1.378	1.408	+2.1*	2.037	2.094	+2.8
1.360	1.394	+2.5	2.836	2.884	+1.7

TABLE 3

Titration of cetyltrimethylammonium bromide with 0.00100 M bromocresol purple in acetate buffer pH 4.62

CTMAB taken ($\times 10^{-3}$ mmol)	CTMAB found ($\times 10^{-3}$ mmol)	Error (%)	CTMAB taken ($\times 10^{-3}$ mmol)	CTMAB found ($\times 10^{-3}$ mmol)	Error (%)
0.482	0.499	+3.5	1.00	0.97	—3.0
0.480	0.499	+4.0	2.00	1.97	—1.5
1.00	1.02	+2.0	2.00	2.00	0.0
1.01	1.04	+3.0	2.50	2.53	+1.2

Titration of cetyltrimethylammonium bromide with bromocresol purple

Cationic detergents form complexes with anionic dyes. These reactions are used in the titrations of detergents [14]. Normally the end-points are determined with the use of an organic solvent immiscible with water, e.g. chloroform. The ion-association complex is insoluble in water and colours the chloroform layer. Both the sample and the titrant of these two-phase titrations generally show tensammetric activity [9]. The feasibility of a tensammetric determination of the end-point will depend on the properties of the complex formed during the titration. From Fig. 5, it can be seen that the adsorption/desorption peak of bromocresol purple at —0.9 V is specific for the free bromocresol purple and can be used to monitor the titration of cetyltrimethylammonium bromide with this compound. Table 3 shows the results of the titration of various amounts of cetyltrimethylammonium bromide with 0.00100 M bromocresol purple. The titrations were carried out in 20 ml of 0.2 M acetate buffer, pH 4.62, at a pulse top potential of —0.9 V and a pulse base potential of 0.0 V at a drop time of 960 ms.

Conclusions

The use of an on-line computer in double-layer capacitance measurements allows routine application of these measurements as a means for the detection of titration end-points. Combination of these measurements with computer control of titrant addition offers an automated technique for the use of titration reactions in which reagents or products are adsorbed at the mercury/

electrolyte interface. The applications given show that this indication method is very useful for monitoring titrations with organic complexing reactions.

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