FAST EVALUATION OF DIFFERENTIAL CAPACITY AND SURFACE CHARGE IN ELECTRICAL DOUBLE LAYERS WITH A.C. OSCILLOPOLAROGRAPHY

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The application of a.c. oscillopolarography for a fast evaluation of differential capacity and surface charge in electrical double layers on the mercury electrode is described. The $C_d = f(E)$, $Q = f(E)$ and $\gamma = f(E)$ functions are displayed. The obtained values of differential capacity and surface charge densities are in agreement with those from the a.c. bridge method. The new method has the distinct advantages of a rapid analytical procedure, visual detection, very simple manipulation and low-cost instrumentation. It is very useful in practical analysis where accurate values of differential capacity and surface charge are not required.
Key words: Polarography; Oscillopolarography; Mercury electrode; Electrochemistry.

Application of the oscilloscope for the study of capacity phenomena on the mercury electrode was already explored many years ago[1–4]. Generally, the triangular voltage sweep and rectangular a.c. pulses were used to polarize the Hg electrode[5–7]. In this paper, we present a very simple method for fast evaluation of the differential capacity and surface charge density in electrical double layers by using a.c. oscillopolarography (ACOP). ACOP is a galvanostatic method introduced by Heyrovský[8,9]. A constant-amplitude alternating current $i = i_0 \sin \omega t$ was passed through an electrolytic cell and the $dE/dt–E$ oscillogram was displayed. It was widely used in microanalysis and electrode process studies[10–13] in the early years of polarography. During the last two decades, novel advancement has been achieved in the practical application of this method[14–19]. We applied this method to the capacity phenomena studies using a home-built device consisting of operational amplifiers combined with a microcomputer for data acquisition. The differential capacity and surface charge densities *vs* potential may be evaluated

easily. Compared with the conventional a.c. bridge approach, the new method possesses distinct merits of simple manipulation, rapid measuring, visual detection and cheap instrumentation.

EXPERIMENTAL

Figure 1 shows a block diagram of the experimental setup. The principle is as follows: A sine wave alternating voltage (f = 50 Hz) is fed from the source (block A) into a constant current source (block B). The constant-amplitude alternating current $i = i_0 \sin \omega t$ is passed through the electrolytic cell (block C). $E – t$ function obtained as output from the cell is fed into the differential circuit (block D) to get dE/dt signal which is further integrated (block E). The signal outputs from points a, b, c and d are fed into a multiple route box[20] (block F) which is used to provide compatibility with digital instrumentation. An oscilloscope (block G) is employed for observing and recording the oscillograms including $C_d = f(E)$, $Q = f(E)$ as well as $\gamma = f(E)$ functions directly. In addition, an IBM microcomputer (block I) is connected to the electrochemical measuring system by an MS-1215 AD/DA interface card (block H) which is used for data acquisition and processing[21]. The program used is written in BASIC language. Sampled data are stored as a file on a floppy disk for future use.

A detailed description of the experimental circuit is shown in Fig. 2. This simple electronic simulator is designed by utilizing operational amplifiers, which in turn embodied many ideas of Peters and Burden[22], Sturrock[23,24], Loveland and Elving[1,2], and from our previous works[25,26]. The essential features of this operational amplifiers circuit for a.c. oscillopolarography have been summarized by Brand and Fleet[27] and Kalvoda[28]. The intensity of the a.c. used for the electrode polarization can be regulated by means of resistance R_2. The current passing through the cell is measured as the effective value of voltage V_R on the resistance R_5 by a multimeter. The a.c. density amplitude i_0 is given by $\sqrt{2}\,V_R/R_5A$, where A is the area of the mercury drop electrode. The value of the d.c. electrode potential ($\bar{E}$) of the electrode is controlled by potentiometer P_1, its magnitude being regulated by the resis-
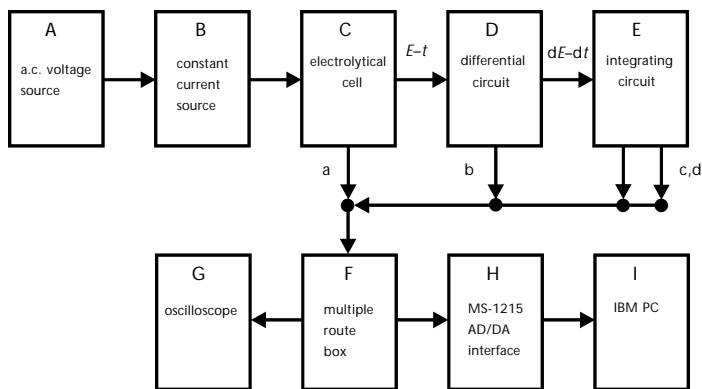

F&#x1D07;G. 1
Block diagram of the electronic apparatus

tance R'_6 and measured with a potentiometer *vs* the saturated calomel electrode (SCE) in the absence of a.c. The application of the d.c. potential should be adjusted in order to obtain well developed curves especially in the negative potential. Capacitances C_1 and C_2 are blocking the d.c. component while L is an inductance separating the a.c. and the d.c. parts of the circuit. A standard three-electrode system is employed. A hanging mercury drop electrode with the area of 0.0302 cm^2 serves as a working electrode, platinum foil (area 4 cm^2) as a counter-electrode and the saturated calomel electrode as a reference electrode. In the differential circuit, U_{o1}, the voltage on the resistance R_7, is proportional to the current, *i.e.*, $U_{o1} = R_7 C_3 (dE/dt)$, where $R_7 C_3$ is the time constant of the differential circuit. Thus we have

$$U_{o1} = U_i = R_7 C_3 (dE/dt) = R_7 C_3 i_0 \sin \omega t / C_d . \tag{1}$$

Combining Eq. (*1*) with the equation $E = \overline{E} - (i_0/\omega C_d) \cos \omega t$ (refs[22,23]) we obtain

$$\text{tg } \omega t = U_{o1}/\{\omega R_7 C_3 (\overline{E} - E)\} , \tag{2}$$

$$C_d = R_7 C_3 i_0 \sin \omega t / U_{o1} . \tag{3}$$

Under the experimental conditions, ω, $R_7 C_3$, E and i_0 are given, the $C_d = f(E)$ curve can be quickly obtained from Eqs (*2*) and (*3*) by measuring each value of the vertical length of the
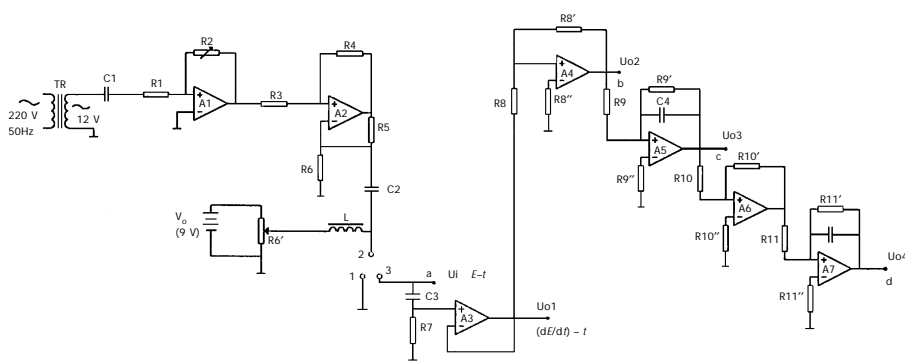

FIG. 2

Circuit diagram for the electronic apparatus. Connections to a cell are: 1 working electrode, 2 counter electrode and 3 reference electrode. TR is a transformer, A_1 to A_7 are operational amplifiers, P_1 is a potentiometer (V_0, R'_6 and L) and V_0 is a dry battery (9 V). Other components have following values: $R_1 = 11$ K, $R_2 = 50$ K, $R_3 = 1$ K, $R_4 = 100$ Ω, $R_5 = 100$ Ω, $R_6 = 1$ K, $R'_6 = 150$ K, $R_7 = 0.950$ K, $R_8 = 0.987$ K, $R'_8 = 100.5$ K, $R''_8 = 0.987$ K, $R_9 = 19.9$ K, $R'_9 = 19.7$ K, $R''_9 = 19.7$ K, $R_{10} = 5.08$ K, $R'_{10} = 99.8$ K, $R''_{10} = 5.11$ K, $R_{11} = 20.2$ K, $R'_{11} = 20.3$ K; $C_1 = 0.47$ μF, $C_2 = 0.47$ μF, $C_3 = 0.01$ μF, $C_4 = 2.83$ μF, $C_5 = 2.55$ μF

trace U_{o1}, corresponding to each certain potential E_i on the dE/dt–E oscillogram. Furthermore,

$$U_{o2} = -(R'_8 / R_8) U_{o1} = -(R'_8 / R_8) R_7 C_3 (i_0 / C_d) \sin \omega t \,, \tag{4}$$

$$U_{o3} = -(1 / C_4 R_9) \int \{-(R'_8 / R_8) C_3 R_7 (i_0 / C_d) \sin \omega t\} dt =$$
$$= -(C_3 R_7 / C_4 R_9)(R'_8 / R_8)(i_0 / \omega C_d) \cos \omega t + k \,. \tag{5}$$

Substituting $\cos \omega t = (\overline{Q} - Q)\, \omega / i_0$ (refs[29,30]) into Eq. (5), we obtain

$$U_{o3} = -(C_3 R_7 / C_4 R_9)(R'_8 / R_8)\{(\overline{Q} - Q) / C_d\} + k \,. \tag{6}$$

If $Q = \overline{Q}$, $k = \overline{U}_{o3}$, then we have

$$U_{o3} = \overline{U}_{o3} - (C_3 R_7 / C_4 R_9)(R'_8 / R_8)\{(\overline{Q} - Q) / C_d\} \tag{7}$$
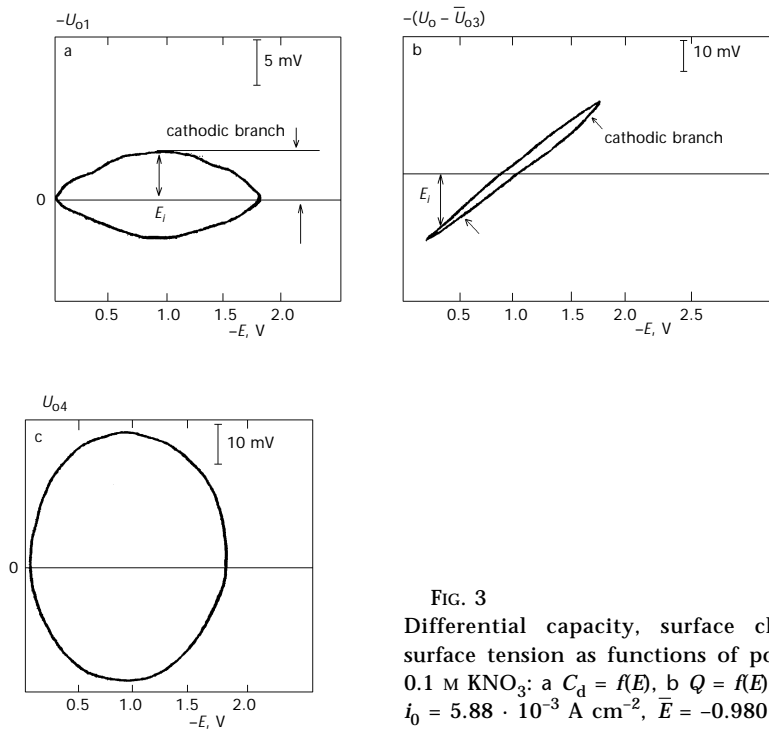

FIG. 3
Differential capacity, surface charge and surface tension as functions of potential for 0.1 M KNO_3: a $C_d = f(E)$, b $Q = f(E)$, c $\gamma = f(E)$; $i_0 = 5.88 \cdot 10^{-3}$ A cm^{-2}, $\overline{E} = -0.980$ V

or

$$Q - \overline{Q} = (C_4 R_9 / C_3 R_7)(R_8 / R_8') C_d (U_{o3} - \overline{U}_{o3}) . \tag{8}$$

Since the values of resistances and capacitances are known, and the C_d is given by Eq. (3), the surface charge density can be easily evaluated by measuring the values of the vertical length of the trace ($U_{o3} - \overline{U}_{o3}$) using Eq. (8). U_{o4} displays the $\gamma = f(E)$ trace. In Fig. 3, there are presented three resulting oscillograms showing differential capacity, surface charge and surface tension *vs* potential for 0.1 M KNO_3.

An experiment started by cleaning of the apparatus. The cell and flasks, kept in aqueous H_2SO_4 (1 : 1), were rinsed with distilled water to remove the trace impurities. The platinum electrode was immersed successively in an aqueous solution of HNO_3 and $(NH_4)_2Fe(SO_4)_2$ (1 : 1) for 10 min and then rinsed with distilled water. All chemicals were of analytical reagent grade. All solutions were prepared using doubly distilled water, deoxygenated for 10 min with pure N_2 and measured at a temperature of 25 ± 1 °C.

The most important factors influencing the accuracy are a.c. density and d.c. potential $\overline{E}$. The optimum d.c. potential ranges from –0.7 to –1.1 V. The magnitudes of i_0 are adjusted just prior to appearance of two bright spots at both the terminal potentials which correspond to the dissolution of mercury and the discharge of cations of the supporting electrolyte. In these cases, no redox reaction occurs on the mercury electrode, the electrode process corresponding to a pure charging process and oscillograms for the given set of conditions are reproducible.

RESULTS AND DISCUSSION

Figure 4 shows an a.c. oscillogram in aqueous 0.1 M KCl. The measurements were done at potentials varying from –0.2 to –1.8 V, the cathodic branch being used. The experimental results indicate that the measured $C_d = f(E)$ and $Q = f(E)$ curves are in good agreement with the data obtained by the a.c. bridge method[31,32] (see Fig. 5).
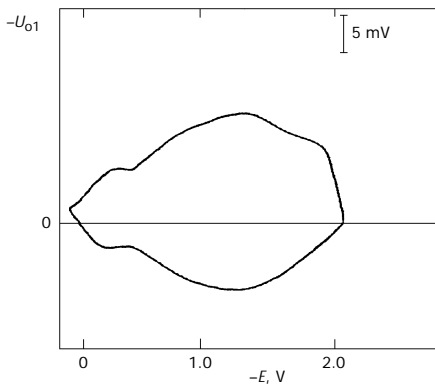

FIG. 4
dE/dt–E oscillogram for 0.1 M KCl: i_0 = 1.38 · 10^{-2} A cm^{-2}, $\overline{E}$ = –0.960 V

Kalvoda[6] brought a similar method for differential capacity measurements. The whole procedure is simplified if the electrode is polarized by a rectangular current. The evaluation of C_d is carried out by comparing the response with a calibration curve measured on the capacitor reference. We have compared our method with Kalvoda's method. Experimental results indicate that in neutral aqueous solution, *e.g.* in 0.1 M NaCl, good results can be achieved with satisfactory precision and accuracy (see Fig. 6). However, in acidic aqueous solution, *e.g.* in 0.1 M HCl, the shapes of the $C_d = f(E)$ is similar to those obtained by Kalvoda's method, but the observed and known values differed by 10 μF cm^{-2} at the most over the potential range of –0.2 to –1.2 V (figure not shown). We believe that this is due to the discharge reactions of H$^+$ on the mercury electrode, resulting in the consumption of current in redox reaction.
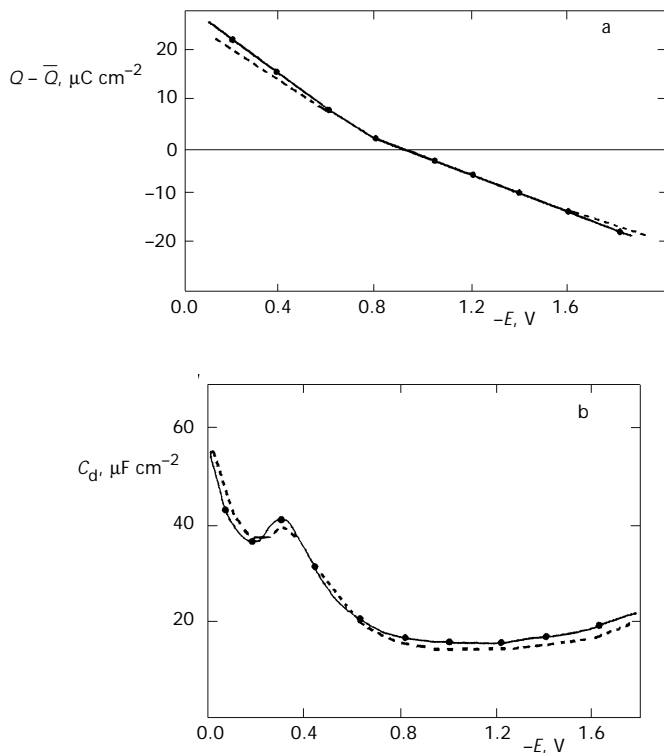

FIG. 5
Surface charge and differential capacity as a function of potential: a $Q = f(E)$ and b $C_d = f(E)$ in 0.1 M KCl; ––––– a.c. oscillopolarography, – – – a.c. bridge method
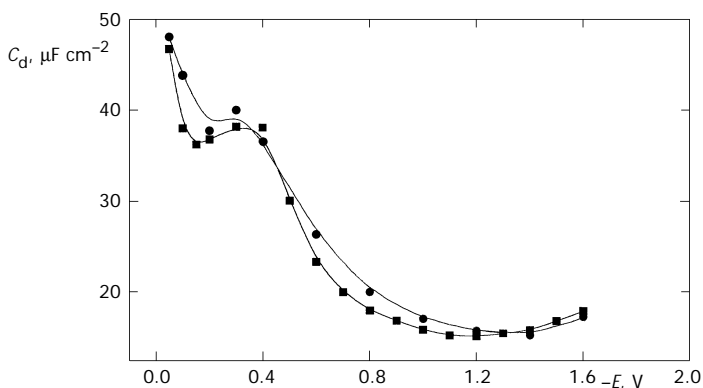
FIG. 6
Differential capacity as a function of potential $C_d = f(E)$ in 0.1 M NaCl: ■ Kalvoda's method, ● oscillopolarographic method; $i_0 = 1.21 \cdot 10^{-2}$ A cm^{-2}, $\bar{E} = -0.834$ V
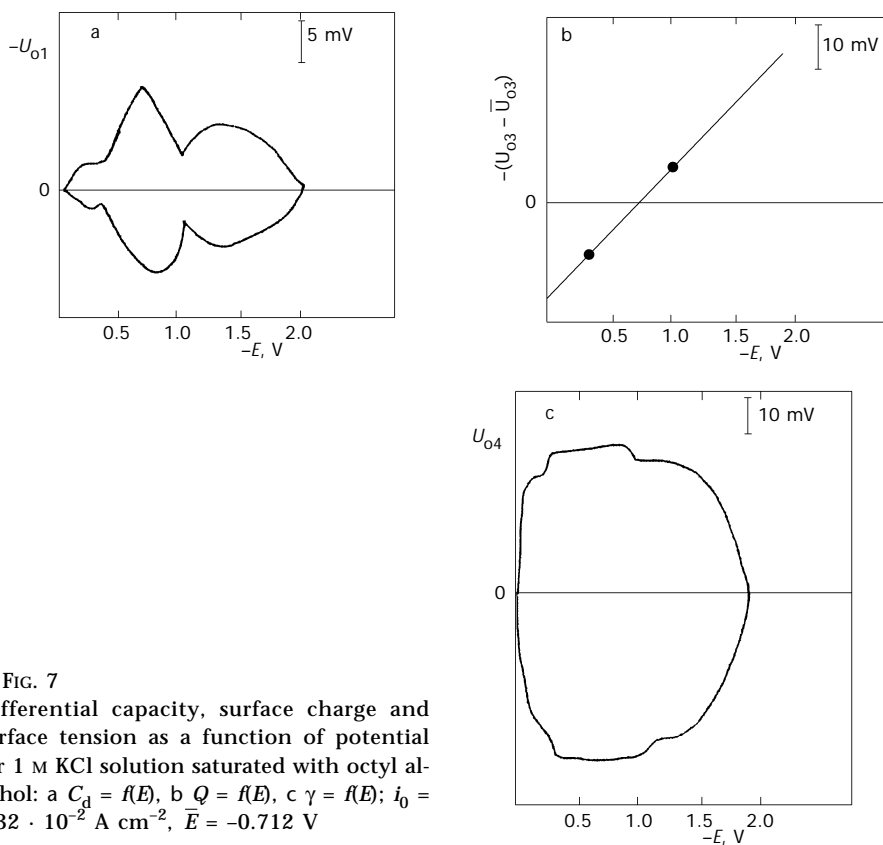

FIG. 7
Differential capacity, surface charge and surface tension as a function of potential for 1 M KCl solution saturated with octyl alcohol: a $C_d = f(E)$, b $Q = f(E)$, c $\gamma = f(E)$; $i_0 = 1.32 \cdot 10^{-2}$ A cm^{-2}, $\bar{E} = -0.712$ V

Adsorption phenomena can also be easily followed by this technique. This is exemplified by the system of 1 M KCl saturated with octyl alcohol (see Fig. 7). In this case sharp indentations are formed on the curve $dE/dt = f(E)$. This observation is in accordance with the results of Kalvoda *et al.*[33]

CONCLUSION

We call this method just evaluation instead of determination because of the assumption of constant electrode capacity in derivation of those equations. The other reason is the assumption that the total injected current is consumed only in charging the electrode, not being influenced by the Faraday current. However, compared with the classic a.c. bridge method, the measuring procedure is considerably simplified. The whole procedure can be finished in only 10 min. The distinct advantage is that $C_d = f(E)$, $Q = f(E)$ as well as $\gamma = f(E)$ functions can be displayed directly on the screen of an oscilloscope. The method is very useful in practical analysis where accurate values of differential capacity and surface charge are not required.

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