THEORY OF POLAROGRAPHY WITH ELIMINATION OF SOME CURRENTS

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A method for the elimination of various components of the polarographic current is proposed, based on its differentiation and/or integration with respect to time and forming a linear combination of the results with the original current. A linear combination of n different functions can be used to eliminate $n - 1$ current components. Examples for the elimination of the charging, diffusion, and kinetic currents are given, and the possibilities of realization and utilization of the new method are discussed.

Elimination of the charging current in polarography, which sets limits to the analytical exploitation of the method, has been dealt with by many authors. Various methods of elimination of the charging current are given in the literature beginning from linear compensation[1], later using measurement of the instantaneous current at the end of the drop time[2,3], integration of the polarographic current[4], and finally measurement of the electrode capacity by the a.c. method and using the result for an electronic compensation[5]. Introduction of further methods, *e.g.* a.c., square wave, and pulse polarography was motivated to a large extent by attempts to suppress the charging current of the dropping electrode and thus to increase the sensitivity of the polarographic method[6-9].

The total polarographic current usually consists of a sum of several components corresponding to different processes, one of which is the charging of the electrode. The problem of elimination of the charging current can therefore be regarded as a special case of a more general problem: elimination of a chosen component from the total polarographic current. Its solution forms the subject of the present work.

THEORETICAL

We assume that the total polarographic current, i, is given by the sum of different components, i_j,

$$i = \sum_j i_j \tag{1}$$

and we want to obtain an expression for the current in which some components are eliminated and another is preserved. Further, we assume that the components i_j are different functions of the time, t, *i.e.*

$$i_j = A_j f_j(t)\,. \tag{2}$$

Here, the coefficient A_j involves some constant parameters. If there are more than one components i_j with the same function $f_j(t)$, they are taken together as one component with a composed coefficient A_j.

The principle of the method of solution of the given problem is that the different functions $f_j(t)$ undergo different changes by differentiation or integration. Hence, if we suitably choose a linear combination of the functions involving the derivatives and/or integrals of the total current, one component is preserved whereas others are cancelled.

To simplify the notation, we use the differential operator $\mathbf{D}$ according to Heaviside, which has the following properties:

$$\mathbf{D}^k i \equiv \mathrm{d}^k i/\mathrm{d}t^k\,, \quad \mathbf{D}^{-k} i \equiv \int_0^t \int_0^t \ldots \int_0^t i\,\mathrm{d}t^k\,, \quad \mathbf{D}^0 i \equiv i\,. \tag{3}$$

A linear combination of the functions involving derivatives and/or integrals of the total current may be written in the form

$$\sum_k g_k(t)\,\mathbf{D}^k i = \sum_j b_j(t)\,i_j\,, \tag{4}$$

where the functions $b_j(t)$ are given as

$$b_j(t) = \sum_k g_k(t)\,(\mathbf{D}^k f_j(t))/f_j(t)\,. \tag{5}$$

Here, k is a positive or negative integer or zero.

If we use n terms in the linear combination with different values of k and determine the functions $g_k(t)$ $(k = 1, 2, \ldots n)$ by solving the system of n equations

$$\sum_k g_k(t)\,(\mathbf{D}^k f_j(t))/f_j(t) = \delta_{nj}\,, \quad j = 1, 2, \ldots n \tag{6}$$

linear with respect to $g_k(t)$, where δ_{nj} is Kronecker's delta, then the functions $b_1(t)$ through $b_{n-1}(t)$ in Eq. (*4*) will be zero, whereas $b_n(t) = 1$. Thus, the components i_1 through i_{n-1} are eliminated from Eq. (*4*), whereas the component i_n remains. Other components beginning from i_{n+1} in Eq. (*4*) are multiplied by time functions $b_j(t)$, which are different from zero.

In a special case, the number of terms with different values of k in the linear combination (*4*) is equal to the number of components in Eq. (*1*). Then, the above procedure leads to the isolation of the component i_n, all other components being eliminated.

In classical polarography, we have usually to deal with functions of the form

$$i_j = A_j t^{\alpha_j}, \tag{7}$$

where t denotes time from the beginning of the drop formation and α_j is a constant which is different for different components i_j. If all components in Eq. (*1*) have this form, Eq. (*5*) may be simplified as

$$\sum_k a_k t^k \mathbf{D}^k i = \sum_j b_j i_j, \tag{8}$$

where a_k and b_j are constants, and

$$b_j = \sum_k a_k \alpha_j!/(\alpha_j - k)!. \tag{9}$$

If the constants a_k are determined for n terms with various values of k by solving the system of n linear equations

$$\sum_k a_k \alpha_j!/(\alpha_j - k)! = \delta_{nj}, \quad j = 1, \ldots, n, \tag{10}$$

then the components i_1 to i_{n-1} in Eq. (*8*) will be eliminated and i_n will be preserved. If the sum (*1*) contains more than n terms, then the values of further coefficients b_j beginning from b_{n+1} are different from zero.

It is noteworthy that when we use more terms with different k values in the linear combination (*8*) than there are different components in Eq. (*1*),then the determination of the constants a_k requires additional conditions (besides conditions of elimination and preservation of the components); *e.g.* not only $b_j = 0$ or 1 for a certain α_j, but also $db_j/d\alpha_j = 0$. All these conditions give a system of equations whose solution gives the values of a_k.

For illustration, several examples are given, where the polarographic current consists of three typical components, namely charging, diffusion, and kinetic currents

$$i = i_c + i_d + i_k, \tag{11}$$

which are given as functions of time[10]

$$i_c = A_c t^{-1/3}, \quad i_d = A_d t^{1/6}, \quad i_k = A_k t^{2/3}. \tag{12)-(14}$$

Here, the coefficients A_c and A_d are proportional to the specific integral capacity of the electrode and to the concentration of the depolarizer, respectively, while A_k involves the depolarizer concentration and parameters of the kinetic process. Since the time dependences are of the form (7), we can use equations (*8*)–(*10*).

If we use a linear combination of two terms, we can eliminate one component. To eliminate the charging current and preserve the diffusion current, we can use the equations

$$\frac{7}{3}\left(i - \frac{2}{3t}\int_0^t i\,\mathrm{d}t\right) = i_d + \frac{7}{5}i_k\,, \tag{15}$$

$$\frac{2}{3}\left(i + 3t\frac{\mathrm{d}i}{\mathrm{d}t}\right) = i_d + 2i_k\,. \tag{16}$$

To eliminate the diffusion current and preserve the charging current, we can use the equations

$$\frac{4}{3}\left(\frac{7}{6t}\int_0^t i\,\mathrm{d}t - i\right) = i_c - \frac{2}{5}i_k\,, \tag{17}$$

$$\frac{1}{3}\left(i - 6t\frac{\mathrm{d}i}{\mathrm{d}t}\right) = i_c - i_k\,. \tag{18}$$

If $i_k = 0$, the above equations can be used to express i_d or i_c.

If we use three terms in linear combination, we can eliminate two components and thus express the third one, *e.g.*

$$(80/9)\left[i - (17/6t)\int_0^t i\,\mathrm{d}t + (65/18t^2)\int_0^t \mathrm{d}t\int_0^t i\,\mathrm{d}t\right] = i_k\,, \tag{19}$$

$$(91/9)\left[(10/3t)\int_0^t i\,\mathrm{d}t - i - (40/9t^2)\int_0^t \mathrm{d}t\int_0^t i\,\mathrm{d}t\right] = i_d\,, \tag{20}$$

$$(20/9)\left[i - (23/6t)\int_0^t i\,\mathrm{d}t + (52/9t^2)\int_0^t \mathrm{d}t\int_0^t i\,\mathrm{d}t\right] = i_c\,. \tag{21}$$

These linear combinations serve merely as examples; others involving different derivatives and/or integrals can be found in the way indicated.

To gain a deeper insight into the method, the dependences of b_j on α_j assuming functions of type (7) and linear combinations (*15*)–(*21*) are shown in Fig. 1. It can be seen that each dependence passes through zero for α_j corresponding to eliminated components, and through unity for α_j corresponding to the component preserved.

DISCUSSION

In experimental realization of the method described, it is suitable to determine the value of the chosen linear combination of functions at a predetermined time t_1. The functions $g_k(t_1)$ and the products $a_k t_1^k$ are then constant, and to obtain the result it is sufficient to differentiate and/or integrate the total polarographic current with respect to time, multiply the results and the current by constant coefficients, adding and/or subtracting, and recording the final value corresponding to time t_1. All these operations can be carried out by an electronic equipment[4,11]. An interesting possibility is that several different linear combinations may be obtained at the same time. Thus, several polarograms with different components of the polarographic current can be recorded on a multichannel recorder. If we choose a linear combination for each polarogram to involve just one component, we obtain a simultaneous decomposition of the polarographic current into its components.

If we consider the polarogram as two-dimensional information, such decomposition represents multidimensional information with a much higher information content.

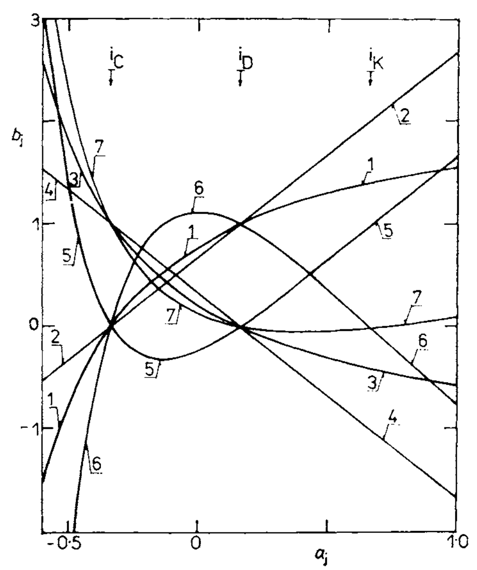

FIG. 1

Dependence of the coefficient b_j on α_j for various linear combinations of functions involving derivatives and/or integrals of the current; time dependence of i_j according to Eq. (7). Curves 1–7 correspond to combinations given by equations (*15*)–(*21*)

To solve the problem of elimination and preservation of certain components of the polarographic current, there are several theoretical possibilities. The selection of the most appropriate equation will depend on a number of circumstances. For example, it is known[4] that integration suppresses noise, whereas the reverse is true for differentiation. Therefore, equations involving integrals seem to be more suitable than those involving derivatives of the current. On the other hand, integrals depend on the total course of the $i - t$ curve, whereas the recorded value of the current and its derivative depends only on a small part of this curve close to the time t_1. If the initial course of the i–t curve is distorted by random effects, equations involving derivatives would therefore be preferable. A detailed analysis of the accumulation of errors arising in electronic circuits during repeated differentiation or integration would possibly lead to limitation of the order of these operations.

It is a general tendency in electrochemical investigations to prefer such methods that rapidly yield the information sought, and not to use methods requiring a number of experiments under various conditions. Polarography using decomposition of the current into its components satisfies this trend. Moreover, it is often polarography which is used first to obtain information about a given system in a broad potential range. The possibility of obtaining more information about the studied process already during the first experimental step could find a broad field of application.

Polarography with elimination of some currents could also find application in analysis, since certain interfering effects can easily be eliminated.

Simultaneous elimination of the charging and kinetic currents, *e.g.*, enables one to determine trace amounts of substances in the presence of interfering kinetic current due to another depolarizer. The separation of the charging current makes it possible to determine surface active substances in the presence of various depolarizers, and the separation of the kinetic current makes it possible to determine substances that give irreversible waves in the presence of an excess of a depolarizer which is reduced reversibly in the same potential region. (Since the current–time curves for an irreversible polarographic wave change from Eq. (*14*) to (*13*) (ref.[12]), the polarogram with a separated kinetic current will show a peak in the potential region of the irreversible polarographic wave.) Hovewer, the sensitivity and the relevant technical problems will have to be evaluated only after practical experience.

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