

# Convulsive Cyclic Voltammetry, Chronopotentiometry, and Digital Simulation Studies of Chloride at a Glassy Carbon Electrode

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**Summary.** The electrode reaction of chloride at a glassy carbon electrode (GCE) in 0.1 M tetrabutylammoniumperchlorate (TBAP)/dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and its electrochemical parameters were determined *via* convulsive cyclic voltammetry and chronopotentiometric (CP) techniques. The parameters calculated from experimental data were tested by comparing the experimental voltammograms with the simulated data. Convulsive cyclic voltammetry was found to provide high sensitivity and better resolution than ordinary cyclic voltammetry.

**Keywords.** Convulsive cyclic voltammetry; Chronopotentiometry; Digital simulation; Kinetic parameters; Experimental voltammograms.

## **Zum Verhalten von Chlorid an einer Glaskohlenstoffelektrode: Konvulsive cyclische Voltammetrie, Chronopotentiometrie und digitale Simulation**

**Zusammenfassung.** Die Reaktion von Chlorid an einer Glaskohlenstoffelektrode (GCE) in 0.1 M Tetrabutylammoniumperchlorat (TBAP)/Dichlormethan ( $\text{CH}_2\text{Cl}_2$ ) und seine elektrochemischen Kenngrößen wurden mittels konvolutiver cyclischer Voltammetrie und Chronopotentiometrie (CP) untersucht. Die experimentellen Ergebnisse wurden durch Vergleich der Voltammogramme mit simulierten Daten überprüft. Konvulsive cyclische Voltammetrie zeigt hohe Empfindlichkeit und ist bezüglich der Auflösung der konventionellen cyclischen Voltammetrie überlegen.

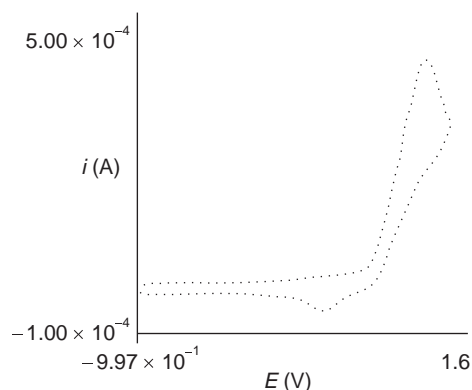
## **Introduction**

Convulsive potential sweep voltammetry was suggested by *Imbeaux* and *Saveant* [1] for the determination of precise reaction mechanisms [1, 2] and also for the estimation of chemical and electrochemical parameters of electrode reactions [3]. The basic concept of convulsive voltammetry is that the concentration of the reactant at the electrode surface, established by diffusion, can be calculated throughout the sweep applied to a stationary electrode. This enables one to use not only some particular points of a voltammetric curve, but the entire voltammogram. It has been found that the electrochemical behaviour of halogen couples depends strongly on the electrolytic solvent [4]. In the present work, cyclic voltammetry,

convolution-deconvolution voltammetry, digital simulation, and chronopotentiometric methods were applied for the investigation and description of the electrochemistry of chloride at a GCE in dichloromethane as well as for the determination of the kinetic parameters of the electrode reaction. The homogeneous rate constant ( $k_c$ ) of the recombination step ( $\text{Cl} \rightleftharpoons 1/2 \text{Cl}_2$ ) was calculated from kinetic convolution ( $I_2$ ). Up to now there have been very few investigations of chloride electrochemistry in  $\text{CH}_2\text{Cl}_2$ , especially *via* convolutive cyclic voltammetry and digital simulation methods.

## Results and Discussion

The cyclic voltammogram of *TBACl* run at 0.2 V/sec with a glassy carbon electrode in 0.1 M *TBAP*/ $\text{CH}_2\text{Cl}_2$  solution against  $\text{Ag}/\text{Ag}^+$  exhibits one anodic current peak (Fig. 1). On the reverse scan there is a cathodic peak related to the anodic peak. The current peaks of the anodic sweeps were found to be proportional to the square root of the potential scan rate ( $v^{1/2}$ ) in the range of 0.05–2 V/sec, indicating that the process is diffusion controlled. The electrode process is found to be electrochemically irreversible as shown by the values of peak differences ( $\Delta E_p = 723$ –826 mV and  $E_p - E_{p/2} = 212$ –272 mV, Table 1).



**Fig. 1.** Cyclic voltammogram of *TBACl* at GCE in  $\text{CH}_2\text{Cl}_2$ ; scan speed: 0.2 V/sec,  $T = 295$  K

**Table 1.** Cyclic voltammetric data of chloride obtained experimentally and theoretically at different scan rates

Scan rate (v/sec)	$E_p - E_{p/2}$ (mV)		$W^p$ (mV)		$\Delta E_p$ (mV)	
	CV	Sim	Decon	Sim	CV	Sim
0.05	212	211	195	194	723	722
0.1	231	229	210	211	760	761
0.2	249	250	226	227	780	780
0.5	254	253	240	242	797	796
1.0	272	271	261	260	826	825

In cyclic voltammetry, the analysis of data is based upon the current and potential values of a few specific points. Often the points of peak or half-peak current are chosen, although these have in fact no special significance compared with the rest of the data through a linear sweep wave. It is much more preferable to use as many data as possible for an effective analysis. A simple mathematical convolution transform method has been proposed for current data [5–8].



In Eq. (1) [3], A is the reduced form, B is the oxidized form, and P is the product of the chemical reaction. The concentrations of A and B at the electrode surface are given by Eqs. (2) and (3) [3]  $n$ : the number of electrons transferred,  $S$ : the electrode area,  $D$ : the diffusion coefficients of A and B which are assumed to be equal to simplify the equations,  $I_1$  and  $I_2$ : given by Eqs. (4) and (5),  $i(u)$ : experimental current,  $u$ : a dummy variable,  $t$ : time calculated from the start of the current).

$$C_{A(0,t)} = C_A^{\text{bulk}} - \frac{I_1}{nFSD^{1/2}} \quad (2)$$

$$C_{B(0,t)} = \frac{I_2}{nFSD^{1/2}} \quad (3)$$

$$I_1 = \frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \quad (4)$$

$$I_2 = \frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)e^{-kc(t-u)}}{(t-u)^{1/2}} du \quad (5)$$

The potential is introduced *via* the *Butler-Volmer* relationship [9] (Eq. (6)) where  $\alpha$  is the transfer coefficient,  $\xi = (E - E^0)nF/RT$ ,  $i_0$  is the exchange current for the electron transfer process at  $E = E^0$ ,  $i_0 = nFSk_f^0 C_A^{\text{bulk}}$ , and  $k_f^0$  is the forward standard heterogeneous rate constant.

$$i = i_0 \left( \frac{C_{A(0,t)} - C_{B(0,t)}e^{-\xi}}{C_A^{(\text{init})}} \right) e^{\alpha\xi} \quad (6)$$

This results in Eq. (7):

$$\frac{I_{\text{lim}}}{i_0} i \cdot e^{-\alpha\xi} = I_{\text{lim}} - I_1 - I_2 e^{-\xi} \quad (7)$$

( $I_{\text{lim}} = nFSC_R^{\text{bulk}} \cdot D^{1/2}$  is the limit of  $I_1$  as  $E$  approaches infinity). This relationship between current, voltage and other parameters holds for all regimes of rates of the electron transfer and the chemical reaction and is in principle suitable for the treatment of data obtained *via* a wide variety of techniques.

In the case of  $\Delta E_p$  beyond  $ca \cdot 300$  mV, the following relationship can be used for the calculation of the standard heterogeneous rate constant  $k_s$  [10]:

$$k_s = 2.18 \left( \frac{D\alpha nFv}{RT} \right) \cdot \exp \left( \frac{\alpha^2 nF}{RT} (E_p^a - E_p^c) \right) \quad (8)$$

The value of  $k_s$  calculated from Eq. (8) is cited in Table 2.

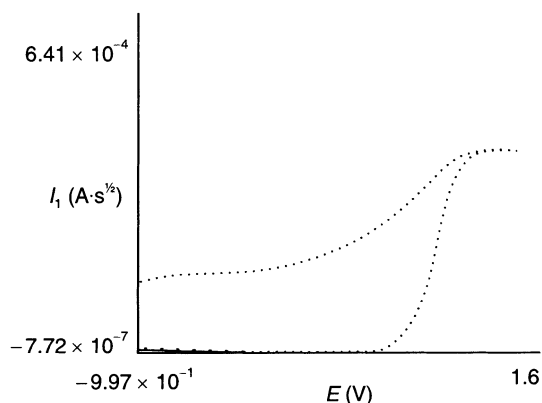


Fig. 2. Convolted current ( $I_1$ ) of TBACl at 0.2 V/sec;  $T = 295$  K

Figure 2 shows the convolted current of the investigated compound at a sweep rate 0.2 V/sec. Convolution analysis of a series of cyclic voltammetric scans obtained using scan rates between 0.05 and 2 V/sec indicate and confirm that the observed behaviour is consistent with a slow electron transfer followed by a chemical reaction due to the mismatch of the return sweep of the convolted current and to the fact that  $I_1$  does not return to zero on completion of the full cycle [11] (Fig. 2). The diffusion coefficient was evaluated from the  $I_1$  convolution using the definition of  $I_{lim}$  and is given in Table 2.

The most accurate and experimentally most attractive route to the evaluation of the rate constant is simply based on a consideration of what would be expected of the surface concentration of the product species (B in Eq. (1)) during the course of a cyclic experiment. If the surface concentration of the product species is examined at a potential well before the electrochemical wave, it will be effectively zero. If the potential is then changed to a point at which some species is produced, its concentration at the electrode surface will rise. Therefore, the procedure for evaluating the  $I_2$  convolution consists in using various test values of  $k_c$  until a value is found that returns  $I_2$  to zero at the end of the cyclic experiment. Diagrammatic examples of the function  $I_2$  evaluated with the true value of  $k_c$  are shown in Fig. 3.

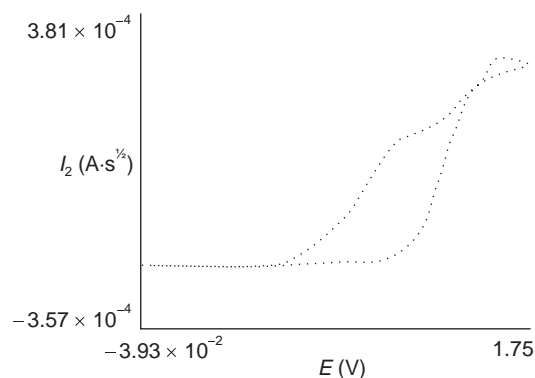
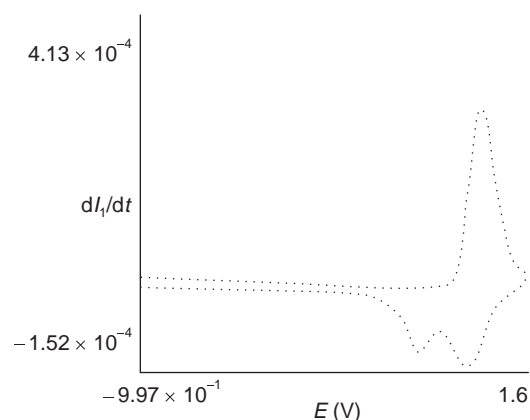


Fig. 3. Kinetic convolution current ( $I_2$ ) of TBACl at 0.2 V/sec,  $T = 295$  K



**Fig. 4.** Deconvoluted current ( $dI_1/dt$ ) of the investigated compound at 0.2 V/sec and  $T = 295$  K

**Table 2.** Electrochemical parameters of chloride in 0.1 M TBAP/ $\text{CH}_2\text{Cl}_2$  via different electrochemical methods

Parameters	Methods				
	CV	Conv	Decon	CP	Sim
$k_s \times 10^8$ (m/sec)	1.7	–	–	–	1.5
$D \times 10^9$ ( $\text{m}^2/\text{sec}$ )	4.21	4.23	4.11	4.10	4.20
$\alpha$	0.34	–	–	–	0.35
$E^0$ (V)	1.136	–	1.134	–	1.131
$k_c$ ( $\text{sec}^{-1}$ )	–	0.076	–	–	0.078

The  $k_c$  value of the chemical step following the electron transfer is found to be  $0.076 \text{ sec}^{-1}$ .

Figure 4 shows the deconvolution of current and potential data. The deconvolution transform gives a rapid assessment of either the electron transfer regime or the value of  $E_{1/2}$ . The asymmetry and inequality of the forward and reverse sweeps confirm the electrochemical nature of the process. Also, the large displacement between the forward and backward sweep of the deconvolution transform (Fig. 4) provides strong evidence for a slow electron transfer [11].

The diffusion coefficient was also determined from deconvolution using Eq. (9) [12] where  $e_p$  is the peak height (in Ampere) of the forward deconvolution sweep and the remaining terms have their usual meanings. The value of the diffusion coefficient estimated from this method is given in Table 2.

$$e_p = \frac{\alpha n^2 F^2 v C D^{1/2}}{3.367 RT} \quad (9)$$

It was found that the half width of the deconvolution current ( $W^p$ ) in the case of fast electron transfer equals 90.53 mV for  $n = 1$  at 298 K [3, 11]. From the values of  $W^p$  given in Table 1 it can be concluded that the rate of the heterogeneous

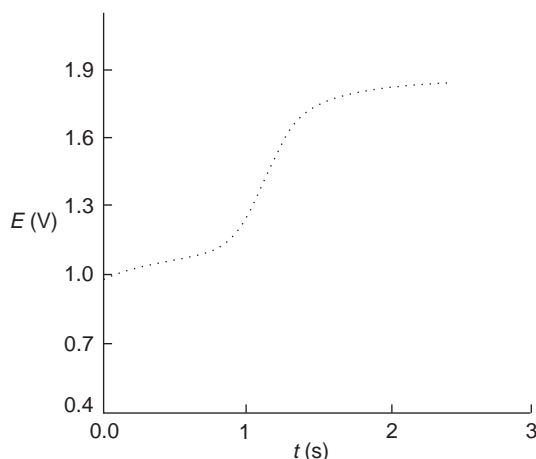


Fig. 5. Chronopotentiogram of TBACl at a glassy carbon electrode ( $T = 295$  K)

electron transfer is slow due to the large deviation of  $W^p$  from the values of fast electron transfer in the case of  $n = 1$  [3, 11]. The reduction potential  $E^0$  was calculated from the average values of the forward and backward peaks (Table 2). The disparity of peak height in the deconvolution (Fig. 4) is an indication of an EC mechanism.

The chronopotentiometric experiment performed with a glassy carbon electrode at 295 K of the compound under investigation displays one oxidation transition time (Fig. 5) which was analyzed *via* Eq. (10) [13] where  $i_c$  is the polarization current and  $t_s$  is the transition time of the investigated compound.

$$I_{\text{lim}} = 2i_c \cdot (t_s/\pi)^{1/2} = (nFSD^{1/2}C^{\text{bulk}}) \quad (10)$$

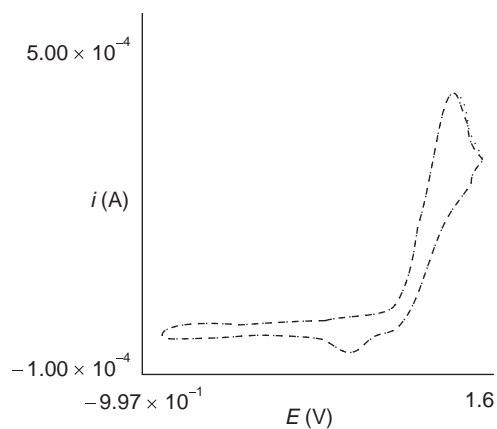
From Eq. (10) the diffusion coefficient was evaluated; it is independent on the rate of electron transfer [14]. The value obtained for the diffusion coefficient from chronopotentiometric experiments was found to be in good agreement with the result obtained from convolution and deconvolution voltammetry.

A direct test of the parameters and the proposed mechanism was performed by generating the following different simulated cyclic voltammograms using the average values of the electrochemical parameters extracted experimentally and comparing them with the experimental one: *i*)  $E_{\text{irr}}$  scheme,  $n = 1$ ; *ii*)  $E_{\text{irr}}$  scheme,  $n = 2$ ; *iii*)  $E_{\text{irr}}C$  scheme,  $n = 2$ ; *iv*)  $E_{\text{rev}}C$  scheme,  $n = 1$ ; and *v*)  $E_{\text{irr}}C$  scheme,  $n = 1$ .

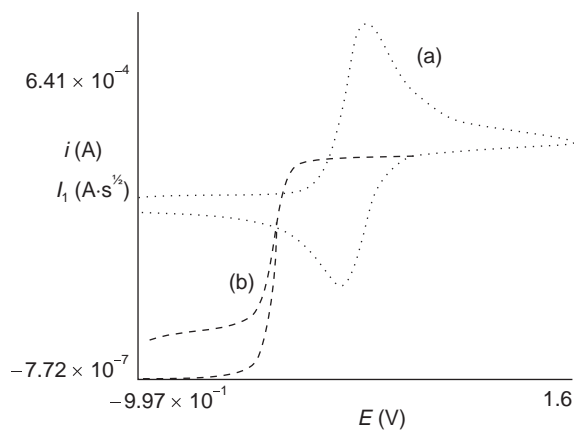
Figure 6 shows a comparison between the simulated voltammogram of type *v* and the experimental one at a scan speed of 0.2 V/sec. There is a good agreement between the theoretical and experimental work which verifies that the moderately fast chemical step is preceded by a single slow electron transfer.

Figure 7 gives an example of the generated cyclic voltammogram and its convoluted current for the  $E_{\text{rev}}C$ ,  $n = 1$  type (*iv*) which confirms the proposed  $E_{\text{irr}}C$  mechanism type (*v*).

According to the above discussion and the interpretation of the electrochemical behaviour, the electrode process of the investigated compound can be suggested to

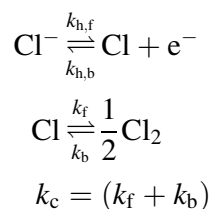


**Fig. 6.** Voltammograms of TBACl at GCE; - - -: experimental, ····: theoretical; scan speed: 0.2 V/sec,  $T = 295$  K



**Fig. 7.** Generated cyclic voltammogram of the  $E_{rev}C$  scheme (a) and convoluted current (b) at a scan speed: 0.2 V/sec

behave as  $E_{irr}C$  mechanism:



## Experimental

The electrochemical measurements were made using a conventional three electrode cell configuration linked to an EG&G model 363 PAR. The glassy carbon electrode (GCE) surface was  $1 \times 10^{-4} \text{ m}^2$ . The auxiliary electrode was composed of a platinum sheet, and the reference electrode was made from silver wire in contact with saturated lithium chloride in  $\text{CH}_2\text{Cl}_2/\text{TBAP}$ .

Digital simulation of the data was performed using the EG&G Condesim package which allows accurate digital simulation for a wide range of mechanisms for cyclic voltammetry.

Tetrabutylammonium perchlorate (*TBAP*) and tetrabutylammonium chloride (*TBACl*) were of polarographic grade and used as supplied (Fluka AG). Fresh solutions of *TBACl* ( $5 \times 10^{-3} M$ ) were prepared in a fresh electrolyte solution ( $0.1 M TBAP/CH_2Cl_2$ ). All working solutions were degassed thoroughly with oxygen free nitrogen, and an atmosphere of nitrogen was maintained above the solutions throughout the course of the experiment. The potential of the working electrode was maintained at a value that no observable current flowed prior to the experiment. All experiments were performed at  $22 \pm 2^\circ C$ .

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