

Determination of Half-wave Potentials of Selected Chlorophenols

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Abstract

Cyclic voltammetry was used in cetyltrimethylammonium bromide (CTAB) micellar solution to determine the half-wave potentials of selected chlorophenols, CPs. It is observed that all the electrochemical parameters of the studied CPs decrease with an increase in the number of chlorine atom(s) attached to the parent compound. The mathematical relationship between the obtained $E_{1/2}$ and the number of chlorine atoms in the parent compound is given. The formal potentials, E^0 , of the CPs are approximated from the obtained half-wave potentials.

Keywords: cyclic voltammetry, half-wave, potential, formal, chlorophenols, electrochemical, parameters.

Introduction

Chlorophenols (CPs) are halogenated phenols. They are used not only as herbicides and bactericides but also in wood preservatives and pharmaceuticals. As a result of their numerous uses, they are eventually released to the environment. They are known to be toxic and listed as toxic chemicals [1]. The EPA has subsequently listed them as carcinogenic [2, 3]. These toxic/carcinogenic chemicals require analytical technique in detecting and detoxifying them. One of the major analytical methods used for detecting and characterizing the CPs is electrochemistry [4-12]. The parameter that is often used is the half-wave potential ($E_{1/2}$) [4-6]. This parameter has been used in quantitative structure-property relationship (QSPR) [13-15] and in correlation with the physical and chemical properties of other compounds [16-19]. $E_{1/2}$ has also been predicted using the quantitative structure-electrochemistry relationship (QSER) [20, 21]. However, to the authors' knowledge, the $E_{1/2}$ has not been used in characterizing the CPs. It is the theme therefore of this work to determine the influence of chloride ion attached to the parent compound, phenol, on the $E_{1/2}$ of

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selected CPs for their characterization. Most CPs are not soluble in water, the experiment in this work is therefore conducted in a micellar solution of 1.0 mM cetyltrimethylammonium bromide (CTAB).

Experimental

Chemical

All the CPs used in this work were all purchased from Aldrich Chemical Co. They are 99.0 % pure or are the purest grade from the manufacturer. A 99.0 % pure CTAB was obtained from Acros Organics. ACS reagent grade potassium chloride (KCl) was obtained from Fisher Scientific Co.

Apparatus

All electrochemical experiments were conducted using a three-electrode system comprising of the working electrode (1.0 mm diameter) Glassy Carbon Electrode (GCE) obtained from Cypress Systems, a wound platinum wire as the counter electrode and a commercial calomel electrode as the reference electrode which was obtained from Fisher Scientific in a 1-compartment electrochemical cell. A computer-controlled electrochemical analyzer system supplied by Cypress Systems, Model CS-10190 was used to obtain the requisite voltammograms of the CPs. The polisher, Metaserv®200, a brown polishing cloth, to resurface the electrode surface and 0.05 micron γ -aluminum powder, used in conjunction with the polishing cloth were obtained from Buehler Ltd.

Methodology

Different amounts of the congeners of cps were weighed into four respective 10.0 mL volumetric flasks containing 0.0110g KCl. The content of the flasks were dissolved and diluted to mark with 1.0×10^{-3} M CTAB. The concentration of each congener was 1.0×10^{-3} M and the concentration of the KCl was 0.15 M. These flasks were then gently sonicated to make the resulting solutions homogeneous before transferring them to the electrochemical cell where they are scanned from 0.0 to 1.2 V. After each scan the electrode surface was renewed by polishing. The CTAB solution was prepared with triply distilled water obtained from Reagent Grade Water System obtained from Photronix.

All the reagents were used as received and the measurements were performed at room temperature, 25 ± 0.2 °C.

Results and discussion

Fig. 1 shows the chemical structure of the CPs studied in this work and the parent compound. Fig. 2 is the forward segment of the cyclic voltammogram of the CPs. As can be seen in this figure, the peak potential and the peak current of the studied CPs are decreasing with an increase in the number of chlorine atoms in each congener. This observation is in accord with what is observed by other workers [22, 23].

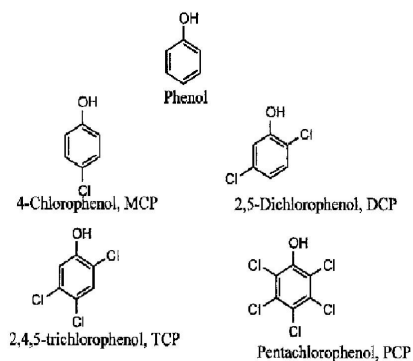


Figure 1. Chemical structures of the studied CPs.

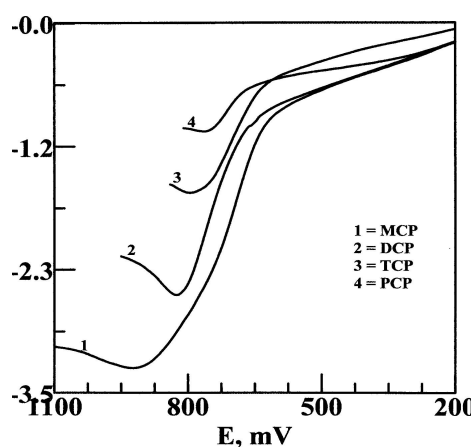


Figure 2. The forward segment of the cyclic voltammogram of the CPs.

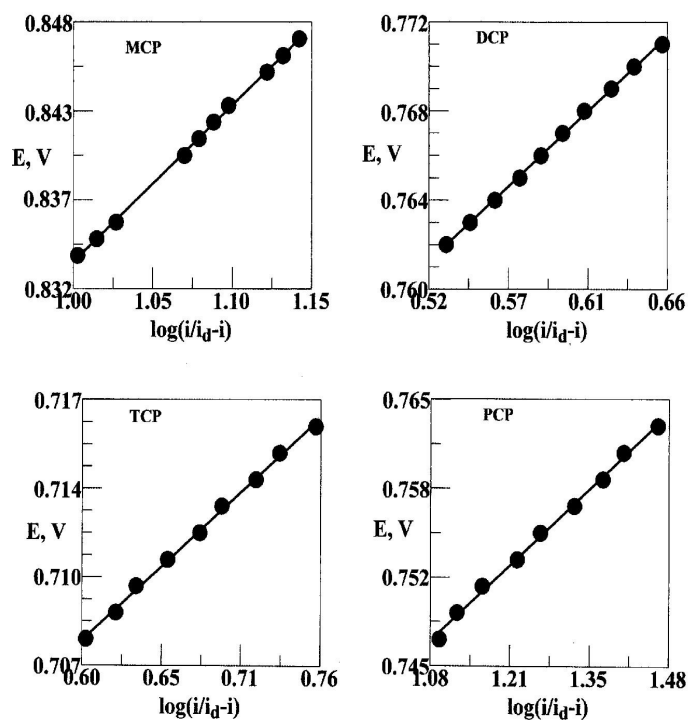


Figure 3. Plots of applied potential, E, versus the logarithm of the resulting current. i_d is the peak current or the diffusion current.

We show in Fig. 3 the usual electrochemical plot of applied potential, E_p , versus $\log(i/i_d - i)$ for the respective congeners which were used in determining the requisite $E_{1/2}$ following the conventional electrochemical technique as given in equation 1.

$$E = E_{1/2} + \frac{RT}{\alpha nF} \log\left(\frac{i}{i_d - i}\right) \quad (1)$$

In this equation R and T are the universal gas constant and temperature in Kelvin scale, respectively. α , n and F are the electron transfer coefficient, the number of electron(s) involved in the reaction and Faraday's constant, respectively. i is the observed current and i_d is the diffusion or peak current. The plots gave intercepts which were taken as $E_{1/2}$.

Table 1 lists the observed peak potential, peak current and the $E_{1/2}$ of the respective congener of the CPs. The observed parameters decrease as the number of chlorine atoms in the phenol is increased. A plot of $E_{1/2}$ versus the number of chlorine atoms is shown in Fig. 4.

Table 1. Observed/calculated electrochemical parameters of the isomers of CP.

Compound	i_p , μA	E_p , V	$E_{1/2}$, V	$\cong E^0$, V
MCP	3.269	0.922	0.74	0.74
DCP	2.588	0.852	0.72	0.72
TCP	1.611	0.789	0.70	0.70
PCP	1.090	0.766	0.68	0.68

i_p = peak current; E_p = peak potential; $E_{1/2}$ = half-wave potential; V = Volts.

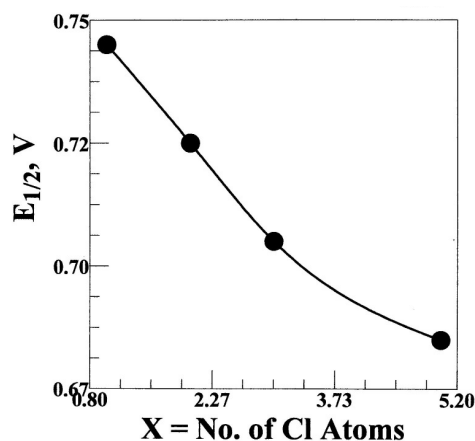


Figure 4. Plot of the observed half-wave potential, $E_{1/2}$, as a function of the number of Cl atoms in each isomer of the CP.

However, this plot is polynomial. We tried several mathematical equations that would be suitable to make the plot linear, in other make the data easy to interpret and its application easier and simpler. We found a good linearity between the $E_{1/2}$ of the respective congener with the square root of the chlorine atoms attached to phenol. Therefore, a plot of $E_{1/2}$ as a function of the square root of the number of chlorine atoms was made (Fig. 5). As can be seen, the plot is quite linear with the coefficient of determination, r^2 , of 0.9926 and a regression coefficient, r , of

99.63%. From this plot a useful mathematical relationship that describes the obtained $E_{1/2}$ of the CPs is:

$$E_{1/2} = 0.787 - 0.049X^{1/2} \quad (2)$$

The X in equation 2 is the number of chlorine atoms. The validity of this relationship can be substantiated by inserting zero for X . When this is done, the $E_{1/2}$ that is obtained in the CTAB solution is 0.79, which is the $E_{1/2}$ for phenol. This value, within an experimental error (uncertainty ± 0.054), is in agreement with what is observed by Yuan and his co-workers (0.799) [14] using the Multiple Linear Regression (MLR) program.

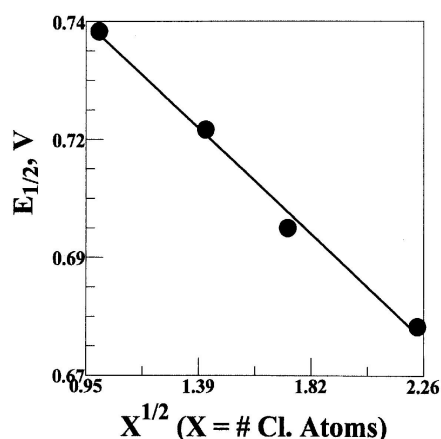


Figure 5. Linearized plot of $E_{1/2}$ versus the square root of the number of Cl atoms in each CP isomer.

The obtained $E_{1/2}$ values of the CPs could be used to approximate their formal potential, $E^{0'}$, in accordance with equation (3) [24]

$$E_{1/2} = E^{0'} + \frac{RT}{nF} \log \left(\frac{D^O}{D^R} \right) \quad (3)$$

In this equation the ratio of the diffusion coefficient of the oxidized specie, D^O , and the reduced species, D^R , is usually unity and $E_{1/2}$ is then approximated to $E^{0'}$ [24]. The $E^{0'}$ thus calculated is also listed in Table 1.

Conclusion

CPs, which are known to be toxic and potentially carcinogenic are insoluble in water, but are relatively soluble in surfactant medium. The surfactant used in this work is cetyltrimethylammonium bromide, CTAB. We have shown in this work that the half-wave potential, $E_{1/2}$, of CPs obtained by cyclic voltammetry in this medium decreases with an increase in the number of chlorine atom(s) attached to the parent compound. A linear mathematical relationship between the observed $E_{1/2}$ of the chlorine content of each isomer of the studied CPs is given and the formal potential, $E^{0'}$, of the CPs is consequently approximated in accordance with the literature.

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