



Electrochemical behavior of dibutyl methyl ester *p*-tert-butyl calix [4] arene

Lilia Tabti¹, Mohamed redha Khelladi^{1,2*},
Embarek Bentouhami^{1,3}

¹LCIMN, Laboratory, University Ferhat Abbas Setif-1, 19000 Sétif, Algeria

²Department of Materials Science, Faculty of Sciences and Technology,
Mohamed El Bachir El Ibrahimi University,
Bordj Bou Arreridj 34030, Algeria

³Department of Process Engineering, Faculty of Technology, University Ferhat
Abbas Setif-1, 19000 Sétif, Algeria

* Corresponding author: Tel./Fax: +213-0794 62 6143; E-mail address:
mohamedridha.khelladi@univ-bba.dz

Article history

Received March 20, 2022

Accepted for publication April 10, 2022

Abstract

The electrochemical behavior of dibutyl methyl ester *p*-tert-butyl calix [4] arene compound 1 was studied by cyclic voltammetry. At 25°C and scan rate of 20 mVs⁻¹. The anodic peak is affected by scan rate, concentration and temperature is a totally irreversible process. The result shows that there is an irreversible electrochemical oxidative wave when the potential is more 1.3 V versus Ag/AgCl in an acetonitrile.

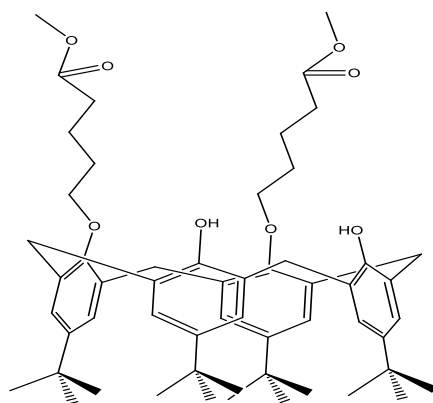
Keywords: Calix[4]arene, Electrochemistry, Cyclic voltammetry, platinum electrode, Diffusion coefficient

1. Introduction

The name calixarenes was introduced by Gutsche [1] for the cyclic oligomers, the use of this word (calix means beaker in Latin and Greek) was suggested in particular by the shape (cup) of tetramer with upper and lower rims and central annulus [2, 3] which are a well-established class of compound in today's in supramolecular chemistry. *p* tert butyl calix[*n*]arenes (*n* = 4, 6, 8) can be easily obtained by the condensation of *P*-substituted phenol and formaldehyde [4,5], can be converted into various derivatives by chemical modifications. Obvious places to

introduce additional functionalities are the phenolic oxygen, which can be converted to ether or ester groups and the *p*-positions. Which are available for all types of electrophilic substitutions after removal of the *t*-butyl groups.[6, 7] Calixarenes and their derivatives have attracted much attention over the past decade as the basis for molecular and ionic recognition because of their conformational and structural flexibility makes them highly attractive platforms for the synthesis of more evolved macro cyclic receptors [8-10] which can be used as ion sensitive electrodes or sensors, optical sensors, chiral recognition devices for solid phase extraction, as a stationary phase and modifiers [11-13].

Scientists always pay attentions to the electrochemical properties of water-soluble calixarenes. For example, Paillert and Diao [9, 10] reported the electrochemical characteristics of *p*-sulfonated calix [6]arene. Guowang Diao and Jing Gu reported the electrochemical properties of *p*-sulfonated calix [4]arene [14] and *p*-sulfonated calix[6]arene [10]. The results showed that both *p*-sulfonated calix[6]arene and *p*-sulfonated calix[4]arene could be oxidized and their anodic waves occurred due to the oxidation of phenolic group. Nevertheless, A few articles reported the electrochemical properties of *p*-tert-butyl calixarenes in organic solvent. Pailleret and al. [15] studied the electrochemical behaviors of both *p*-tert-butyl calix [4]arene and *p*-tertbutyl calix[6]arene in dichloromethane . Pailleret and Arrigan. [13] reported the electrochemical oxidation of tetra ester calix [4]arene in acetonitrile In this article, we are interested in examining the electrochemical behavior of dibutyl methyl ester *p*-tert-butyl calyx [4] arene . The results show there is two peak anodic waves when the potential ranges from -0.1 to 2.0 V versus Ag/AgCl, due to the oxidation of the dibutyl methyl ester *p*-tert-butyl calix [4] arene.



Scheme 1. Chemical structure of compound 1.

2. Experimental

Compound 1, dibutyl methyl ester *p*-tert-butyl calix [4]arene . Was prepared according to literature methods [16, 17] Solutions of this compound are prepared in acetonitrile with the background electrolyte tetrabutyl ammonium perchlorate (0.1 M). This was synthesized according to House et al. [18]. The electrolyte solution was deoxidized by bubbling with nitrogen for 10 min prior to performing the electrochemical measurements. The conventional electrochemical measurements were taken using a glass cell consisting of a three-electrodes assembly that was connected to a VoltaLab 40 (PGZ301 & Volta Master 4) controlled by a personal computer. The counter electrode was a platinum wire (10 mm) the working electrode was a platinum disk (2 mm) and the reference electrode was (Ag/AgCl, 8 mm) in organic phase. The working electrode was rinsed in water, then acetonitrile and allowed to dry in air before use.

3. Results and Discussion

The electrochemical behaviors of compound **1** on Ag/Ag⁺ were investigated by cyclic voltammetry. At scan rate of 20 mVs⁻¹ and 25°C, the cyclic voltammogram of compound **1** is 5×10⁻⁴M + 0.1M TBAP in acetonitrile is shown in Figure 1 (the solid line red). The background (the solid line black) is also shown in Figure 1. No electrochemical reaction occurs in the blank buffer solution containing compound **1** in our experimental potential window. It is clear that there is two anodic waves observed when the potential is scanned from -0.1 to 2.0 V versus Ag/Ag⁺, the first peak potential is 1.48 V. Compared with *p*-tert-butyl calix [8]arene and phenolic calixarenes The first conclusion to draw from these observations is that the phenol moieties of parent calixarenes are electrochemically active in organic media, as expected from the known electroactivity of phenols [16, 19]. The second peak potential observed is 1.80V, due to the oxidation of the hydroxyl group [20].

The voltammograms of compound **1** recorded in multi-cycles are shown in Figure 2 at a scan rate of 20 m Vs⁻¹. Repetitive potential cycling do not show any substantial alteration of the initial intense and irreversible oxidation peak upon repeated potential cycling this indicates that electrochemical oxidation of compound **1** are oxidisable but did not passivate the electrode surface [20].

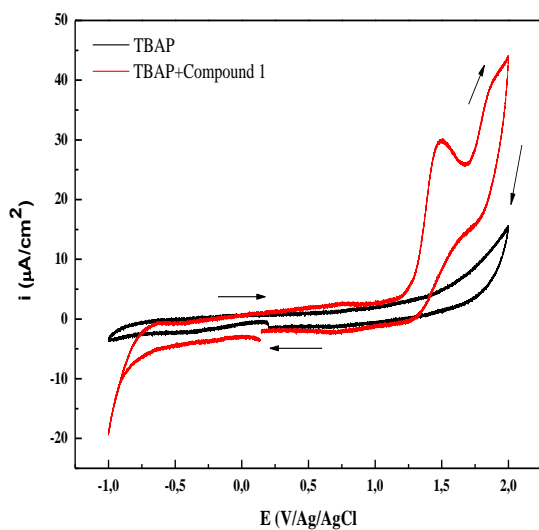


Figure 1. The voltammograms of the background and the solution containing 5×10^{-4} M compound 1 + 0.1M TBAP in acetonitrile at scan rate of 20 mVs^{-1} and 25°C .

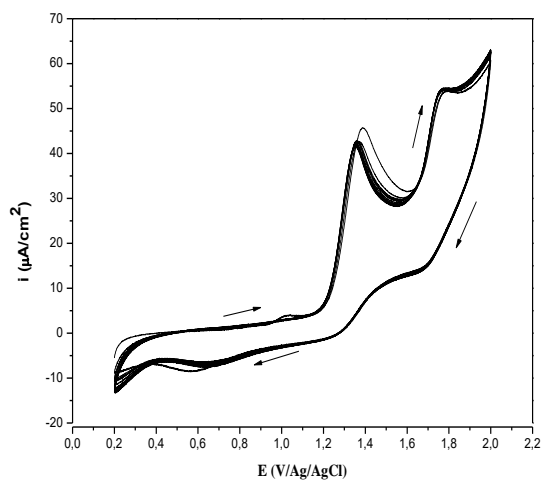


Figure 2. The voltammograms for multi-cycles of 5×10^{-4} M compound 1 in acetonitrile at scan rate of 20 mVs^{-1} and 25°C .

3.1 Measurements of n , D_R , and α

At 25 °C, As shown in **Figure 3**, both anodic peak potential, E_p and peak current, i_p are affected by the scan rate, v . According to Nicholson [21], for an irreversible anodic reaction, the relationship between E_p and $\ln v$ is linear, and can be described as follows:

$$E_p = E^\circ + \frac{RT}{\alpha n_a F} + \left[0.780 + \ln \left(\frac{D_R}{K^\circ} \right)^{\frac{1}{2}} + \left(\frac{\alpha n_a F}{RT} \right)^{\frac{1}{2}} \right] \quad (1)$$

where E° is the formal standard potential, R the gas constant, n_a the number of the electrons transferred in the rate determining step, α the electron transfer coefficient, F the Faraday constant, T the absolute temperature. D_R diffusion coefficient of compound 1, T the absolute temperature, and K° the standard heterogeneous reaction rate constant.

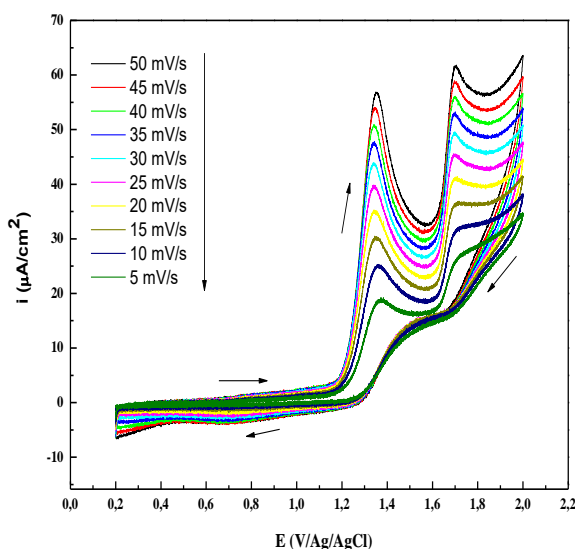


Figure 3. The voltammograms of 5×10^{-4} M compound 1 + 0.1M TBAP in acetonitrile at different scan rates with 25°C.

According to the slope of the straight line of E_p against $\log v$, is shown in Figure 4. The product of α and n_a can be evaluated as 1.29.

The peak current i_p for an irreversible electrochemical reaction can be described as follows [21]

$$i_p = (2.99 \times 10^{-5}) n (\alpha n_a)^{\frac{1}{2}} \times A C_R D_R^{1/2} V^{1/2} \quad (2)$$

Where n represents the number of electrons transferred in the electrochemical reaction, A the area of the electrode, C_R the initial concentration of compound 1.

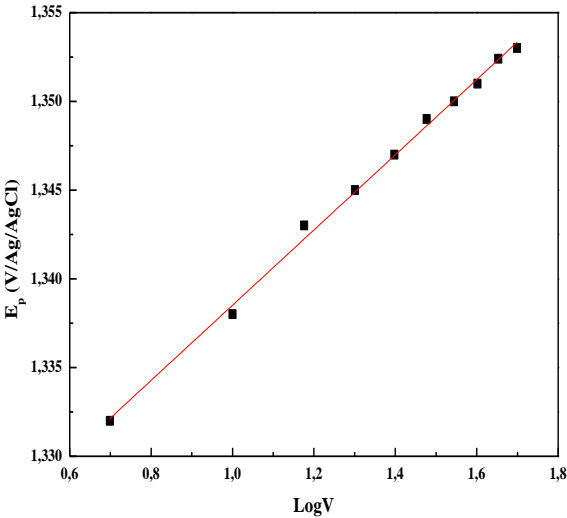


Figure 4. The plot of the anodic peak potential and the natural logarithm of the scan rate. The experimental conditions are the same as these described in figure 3.

According to Eq. (2), at a given initial concentration of III, the plot of i_p versus $V^{1/2}$ must be straight line. Figure 5 shows the experimental results. From the slope of the straight line, can be evaluated the value of $\left(n(\alpha n_a)^{\frac{1}{2}} \times D_R^{1/2}\right)$ in $1.7 \times 10^{-3} \text{ cm s}^{-1/2}$

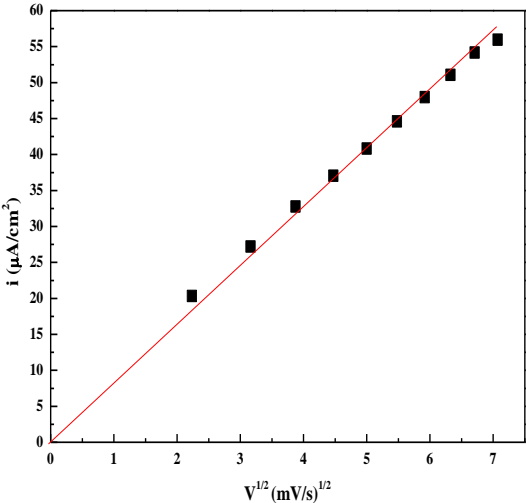


Figure.5. The relationship between the peak current i_p and the square root of scan rate $V^{1/2}$. The experimental conditions are the same as these described in figure 3.

Figure 6. presented the voltammograms at different concentrations of compound 1. The value of $\left(n(\alpha n_a)^{\frac{1}{2}} \times D_R^{1/2}\right)$ can also be obtained by plotting i_p versus the concentration, C_R of compound 1 according to a scanning rate, at 20 mVs^{-1} the straight lines between i_p and C_R are plotted and are shown in Figure 7. According to the slopes of these lines, can be calculated the values of $\left(n(\alpha n_a)^{\frac{1}{2}} \times D_R^{1/2}\right)$ as $1.6 \times 10^{-3} \text{ cm s}^{-1/2}$.

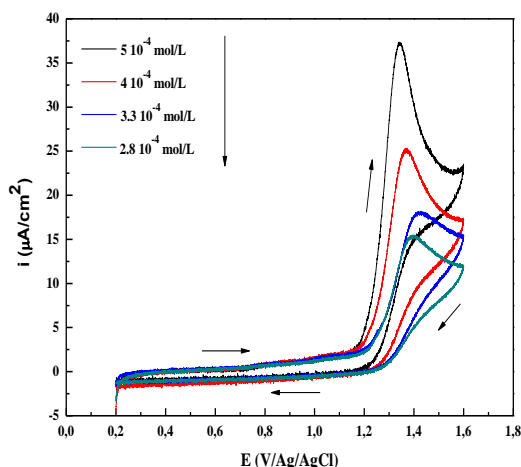


Figure 6. The votammograms of compound 1 at different concentration, 25°C and 20 mVs^{-1} .

The error for both results calculated is located within the mistake of our experiments bar. The mean value is $1.65 \times 10^{-3} \text{ cm s}^{-1/2}$, that is the same as that measured by plotting i_p versus $V^{1/2}$. As described formerly, the value of αn_a is 1.29. Combination of two settings αn_a and $\left(n(\alpha n_a)^{\frac{1}{2}} \times D_R^{1/2}\right)$ we can obtain the value of the product of n and $D_R^{1/2}$ the value of $nD_R^{1/2}$ is calculated as $1.47 \times 10^{-3} \text{ cm s}^{-1/2}$.

For determining the value of n and D_R , a steady state voltammogram was measured by a platinum disc microelectrode (diameter: 2 mm). Was determined and represented in Figure 8. The limited current diffusion, it is measured as $0.51 \mu\text{A}$. The value of nD_R is calculated as $0.2 \text{ cm}^2 \text{ s}^{-1}$ by using the relationship $i_l = 4nFD_R C_R$ [20], the diffusion coefficient, D_R of compound 1 may be evaluated as $6.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and n , the number of electrons transferred in the electrochemical oxidation of compound 1, n is taken as 2, which is greater than that of p -sulfonated sodium salt of calix [6] arene in solution studied [10]. The result shows that it is advantage for the electrochemical oxidation of calixarene in organic solvent.

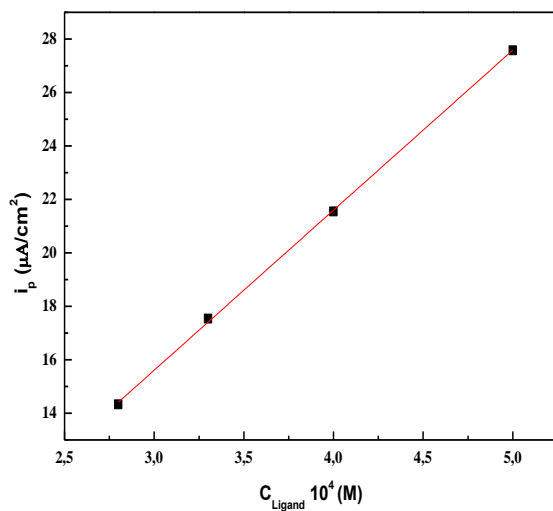


Figure 7. At 25°C, the relationships between I_p and the concentration of compound 1.

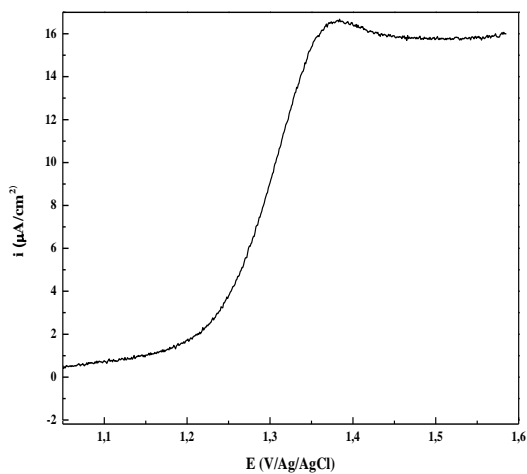


Figure 8. The steady state voltammograms of compound 1 on a platinum disc electrode with scan rate of 5 mVs^{-1} . The other experimental conditions are the same as those described in figure 3.

3.2 Temperature dependence

At different temperature, the voltammograms of compound 1 are presented in Figure 9. The anodic peak current increased with the temperature. At higher temperature, the peak potential shifts in the negative direction, this means that it is easier for the oxidation of compound 1 [14, 19].

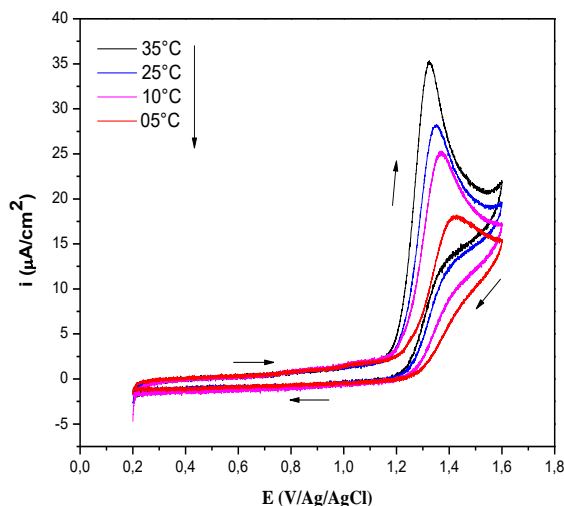


Figure 9. The voltammograms of compound 1 on platinum disc electrode with scan rate of 5 mVs⁻¹ at different temperature.

4. Conclusion

In acetonitrile, compound 1 can be oxidized on platinum electrodes. The anodic peak potential is observed as 1.48 and 1.74 V (versus Ag/AgCl) at 25° C. The result shows that there is an irreversible electrochemical oxidative wave. The number of the electrons transferred in the electrochemical reaction is 2. The diffusion coefficient of compound 1 is $6.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

References

- [1] C.D. Gutsche, *Calixarenes Revisited*, Royal Society of Chemistry: Cambridge (1998).
- [2] V. Bohmer. Chem. Int. Ed **34** (1995) 713-745.
- [3] S. Bouhroum, J.S. Kim, S.W. Lee, P. Thuéry, G. Yal, F. Arnoud-Neu, J. Vicens, J. Incl. Phenomen. Macrocycl. Chem **62** (2008) 239-250.
- [4] B.S. Creaven, D.F. Donlon, J. Mogninley, Coord. Chem. Revi **253** (2009) 893-962.
- [5] J. Schatz, F. Schildbach, A. Lentz, S. Rastatter, J. Chem. Soc. Perkin Trans **2** (1998) 75-78.

- [6] G. Gormar, K. Selffarth, M. Schulz, J. Zimmermann, G. Flamig, Die Makromol. Chem **191**(1990) 81-87.
- [7] C. Gruttner, V. Bohmer, Tetrahedron Letters **35** (1994) 6267-6270.
- [8] Y. Wu, S. Zhai, L. Qiang, L. Gao, F. Wang, J. Chin. Chem. Soc **62** (2015) 342-348.
- [9] A. Pailleret, N. Magan-Oliva, S. Ollivier, D.N.M. Arrigan. J. Electroanal. Chem **508** (2001) 81-88.
- [10] G. Diao, Y. Liu, Electroanalysis **17** (2005) 1279-1284.
- [11] V.V. Egorov, Y.V. Sinkevich, Talanta **48** (1999) 23-28.
- [12] C. Lynam, K. Jennings, D. Diamond, Anal. Chem **74** (2002) 59-66.
- [13] Mc.G. Mohan, S.O. Malley, K. Nolan, D. Dianond, Arkivoc **7** (2003) 23-31.
- [14] G. Diao, W. Zhou, J. Electroanal. Chem **15** (2004) 325-330.
- [15] A. Pailleret, G. Herzog, D.W.M. Arrigan,. Electrochem.Com **5** (2003) 68-72.
- [16] M.A. Mckervery, E.M. Seward, G. Ferguson, B. Rull, S.J. Harris, J. Chem. Soc. Chem. Commun (1985) 388-390.
- [17] F. Arnaud-Neu, E.M. Collins, J. Am. Chem. Soc **111** (1989) 8681-8691.
- [18] H.O. House, E. Feng, N.P. Peet, J. Org. Chem **36** (1971) 2371-2375.
- [19] G. Diao, J. Gu, J. Electrochim. Acta **52** (2006) 42-46.
- [20] R. Vataj, A. Louati, C. Jeunesse, D. Matt J. Electroanal. Chem **565** (2004) 295-299.
- [21] A. J. Bard, L. R. Faulkner, Electrochemical Methods-Fundamentals and applications, 2nd Ed., Wiley, New York (2001).