Int. J. Electrochem. Sci., 16 **(2021)** 151016, doi: 10.20964/2021.01.11

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Behavior of the Facilitated Transfer of K^+ by Dibenzo-18-Crown-6 at the water|1,2-dichloroethane Interface in the Presence of Bisphenol A

E. Martínez Hernández[1], *J. Amador-Hernández*[1], *R. Antaño López*[2], *E. M. Colunga Urbina*[1],
I. M. de la Garza Rodríguez[1] *and M. Velázquez-Manzanares*[1,*]

[1] Facultad de Ciencias Químicas, Universidad Autónoma de Coahuila, Saltillo Coahuila, 25280, México.
[2] CIDETEQ,S.C. Parque Tecnológico Querétaro, Sanfandila, Pedro Escobedo, Querétaro, 76703, México.
[*]E-mail: mvmiguel@hotmail.com; miguel_velazquez@uadec.edu.mx

Received: 8 September 2020 / *Accepted:* 26 October 2020 / *Published:* 30 November 2020

The present work examines the influence of bisphenol A on the facilitated transfer of K^+ by dibenzo-18-crown-6 across the water|1,2-dichloroethane interface. Electrochemical studies are conducted by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). The results indicate that bisphenol A does not partition into the aqueous phase, but remains at the interface, where it inhibits the phase-transfer of K^+. The transfer current of this cation decreases as the concentration of bisphenol A in the organic phase increases. CV and EIS studies indicate that bisphenol A absorbs on the organic side of the interface, where it decreases the active area and blocks K^+ transport. The results of this work can serve as a model to understand interfacial ion transfer in biological membranes and the potential behavior of BPA in living systems.

Keywords: ITIES, AC impedance, DB18C6, Bisphenol A, Ion Transfer

1. INTRODUCTION

The interface between two immiscible electrolyte solutions (ITIES) often is used to study the electrochemical behavior of biomolecules at liquid|liquid interfaces. Molecules examined include heparin [1,2], protamine [3], hemoglobin [4], insulin [5], and dopamine [6-8] The ion transport that occurs in this environment can be likened to the behavior of ion transport across biological membranes. Thus, there are important ramifications to understanding the physicochemical parameters that govern the transfer of molecules across an ITIES.

Hydrophobic ligands facilitate the passage of ions across an ITIES, because they reduce the energy required to transfer a charged species across a water|oil interface. Studies have been conducted on the facilitated transfer of ions including Na^+, Li^+, Cs^+, Rb^+, and K^+ using ligands such as crown ethers [9]. ITIES is an important tool for understanding facilitated ion transfer, because it is a readily simulated process.

The study on facilitated potassium ion transfer dates to the 1979 report of Koryta, who studied K^+ transport assisted by the dibenzo-18-crown-6 ionophore (DB18C6) across a water|nitrobenzene interface [10]. The presence of an ionophore in the organic phase reduces the Gibbs free energy for potassium ion transfer by a complexation reaction at the water|organic solvent interface. Electrochemical analysis of facilitated K^+ transfer has been conducted by cyclic voltammetry and Electrochemical Impedance Spectroscopy [11,12].

ITIES also has been used to quantitate ions and organic compounds. It is a sensitive and practical analytical technique. For example, 0.12 μM ammonium ion has been detected by ITIES using cyclodextrin as a complex agent [13]. Heparin adsorption and desorption has been used as a means of its detection by stripping voltammetry using ITIE [1]. The detection of metoprolol in human biofluids employed nano-ITIES arrays [14]. γ-Aminobutyric acid has been detected by an ITIES supported on the orifice of a pipet [15]. Acetylcholine, tryptamine, and serotonin also have been analyzed [16]. Ion transfer across an ITIES can be used in multiple applications, but the process of ion-transfer blocking at an interface is helpful in developing pharmaceutical products that inhibit the actions of poisons and pathogens [17].

Adsorption phenomena at a water|1,2-dichloroethane interface have been investigated by EIS through studies of long-chain phospholipids including distearoyl-phosphatidylcholine (DSPC), dioleyl-phosphatidylcholine (DOPC), dilauril-phosphatidylcholine (DLPC), dimiristoyl- phosphatidylcholine (DMPC), and dipalmitoyl-phosphatidylcholine (DPPC). These lipids form a compact monolayer at the ITIES, the concentration of which influences the ionic partitioning process [18]. The kinetics of acetylcholine transfer across at the water|1,2-dichloroethane (DCE) interface modified with dipalmitoyl-phosphatidylcholine (DPPC) illustrate this behavior. The presence of the DPPC monolayer inhibits acetylcholine transfer at the interface, which results in a decrease in the apparent rate constant of ion transfer with increasing lipid concentration [19]. Our group has studied the transfer of the herbicide metamitron across a water|1,2-DCE interface modified with a L-α-phosphatidylcholine monolayer [20]. The lipid monolayer enhances transfer of the herbicide when a perfect layer is formed, but in this case there is no decrease in the active interfacial area between the two liquids.

Bisphenol A (BPA) is an organic compound widely used as a plasticizer in many products encountered in daily life, including personal care products, CDs, epoxy resins, and food containers [21, 22]. BPA bioaccumulates in organic tissues and blocks the transport of ions through plasma membranes. Considerable attention has recently been directed to its estrogenic activity, which is present even at concentrations below 1 mg L^{-1} [23]. The objective of our current work, which is based on this connection, is to study the effect of BPA on the transfer of potassium ions across the interface between two immiscible electrolyte solutions.

2. EXPERIMENTAL

A four-electrode cell configuration with an interfacial area of 0.35 cm^2 was used. The cell contained two platinum counter electrodes (Sigma-Aldrich, 99.9% purity) and two silver reference electrodes. Cyclic Voltammetry (CV), Square Wave Voltammetry (SWV), and Electrochemical Impedance Spectroscopy (EIS) experiments were conducted with a Reference 600 potentiostat/galvanostat (Gamry Instruments, USA).

The reagents used included KCl (J.T. Baker), dibenzo-18-crown-6 and 1,2-dichloroethane (Sigma-Aldrich), and triply distilled water (Jalmek, Mexico). Tetraphenylarsonium chloride (TPAsCl, Aldrich) and tetraphenylarsonium tetrakis-4-chlorophenylborate (TPAsTPBCl, Aldrich) were employed as the reference and supporting electrolyte, respectively, in the organic phase. TPAsTPBCl was prepared from TPAsCl and potassium tetrakis-4-chlorophenylborate (Fluka, purum). The TPAsTPBCl precipitate was recrystallized twice from acetone (J.T. Baker). Bisphenol A (Figure 1) was obtained from Sigma-Aldrich.

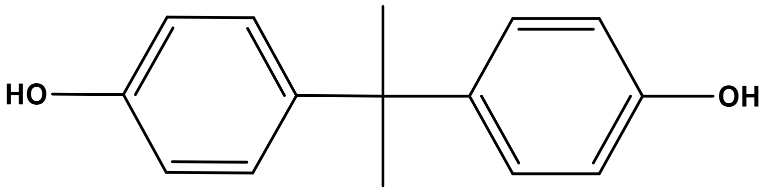

Figure 1. Chemical structure of BPA.

The cell construction is represented as follows:

$$\begin{array}{lclclclcl}
\mathrm{Ag|AgCl_1} & | & \mathrm{TPAsCl} & | & \mathrm{TPAsTPBCl} & |\Theta| & \mathrm{KCl} & | & \mathrm{Ag|AgCl_2} \\
 & & 0.02\mathrm{M} & & 0.02\mathrm{M} & & 0.05\mathrm{M} & & \\
 & & & & \mathrm{DB18C6} & & & & \\
 & & & & \mathrm{BPA} \neq \mathrm{mX} & & & &
\end{array}$$

where mX is the concentration of BPA in the organic phase, ɵ is the interface under investigation, and Ag|AgCl$_1$ and Ag|AgCl$_2$ are the reference electrodes. The potential on the Galvani scale is calculated as follows:

$$E_{cell} = \Delta_o^w \phi - \Delta_o^w \phi_{TPAs^+} \qquad (1)$$

where $\Delta_o^w \phi$ is the interfacial Galvani potential and $\Delta_o^w \phi_{TPAs^+}$ is the potential of the organic phase reference ion, which is assumed to be –0.364 V.

3. RESULTS AND DISCUSSION

3.1 Cyclic Voltammetry

Figure 2 shows a cyclic voltammogram for the facilitated transfer of K^+ by DB18C6 across the water|1,2-dichloroethane (1,2-DCE) interface. The baseline established by the supporting electrolytes (dotted line) creates a potential window of −0.24 to 0.34 V. Free ions require considerable energy to be transferred from the aqueous to organic phase at an ITIES. In fact, K^+ transport into the organic phase requires approximately 50 kJ mol^{-1} [24] and takes place at the edge of the potential window. Therefore, the peak attributable to the transfer of this cation occurs near the potential where $TPBCl^-$, which is the anion of the supporting electrolyte in the organic phase, is transferred into the aqueous phase.

When DB18C6 is injected into the organic phase and the interface is polarized, the current for facilitated K^+ transfer is brought into the middle of the potential window as previously observed [10]. The explanation for this is that the DB18C6 ligand decreases the energy required to transport the cation into the organic phase. If the interface is polarized in the positive direction, a current peak is observed at 0.01 V. This indicates that K^+ is transferred from the aqueous to the organic phase by an interfacial complexation reaction. When polarization is imposed in the opposite direction, a negative current peak is observed at −0.056 V, which is attributed to the transfer of K^+ from the organic phase to the aqueous phase by an interfacial decomplexation reaction.

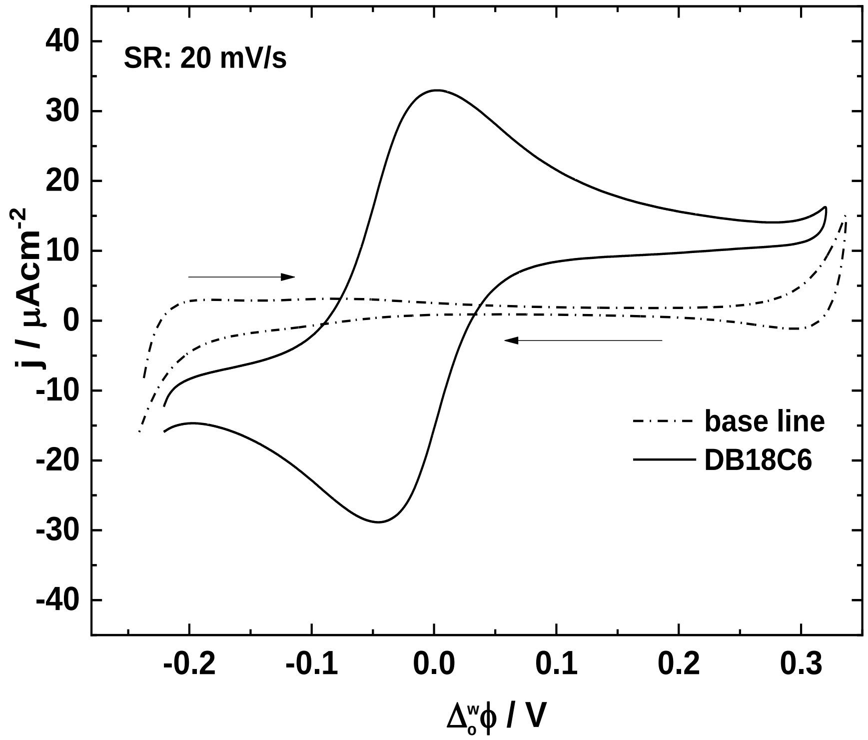

Figure 2. Facilitated Transfer of K^+ by DB18C6 (0.14 mM) across the water|1,2-DCE interface (solid line). Supporting electrolyte: TPAsTPBCl 0.01 M in the organic phase and KCl 0.05 M in the aqueous phase (dotted line).

Assuming that the half wave potential, $\Delta_o^w\phi_{1/2}$ = -0.023 V, an assuming that the $\Delta_o^w\phi_{1/2} \approx \Delta_o^w\phi_{LK^+}^{0\prime}$ is an equilibrium value and that the Gibbs energy ($\Delta_o^w G_{LK^+}^{0\acute{}w\rightarrow o}$):

$$\Delta_o^w G_{LK^+}^{0\acute{}w\rightarrow o} = zF\Delta_o^w\phi_{LK^+}^{0\prime} \tag{2}$$

where z is the charge, F is the Faraday constant, and $\Delta_o^w\phi_{LK^+}^{0\prime}$ is the formal transfer potential. The result is $\Delta_o^w G_{LK^+}^{0\acute{}w\rightarrow o}$= -2.21 kJ mol^{-1}. The peak-to-peak separation of 66 mV is close to the 59 mV value established by the Nernst equation for a reversible reaction involving transfer of a single unit of charge. The reaction for the phase transfer of K$^+$ in the presence of a largely hydrophobic ligand is written as:

$$K_{(w)}^+ + L_{(o)} \rightleftarrows LK_{(o)}^+ \tag{3}$$

where $L_{(o)}$ is the DB18C6 ligand in the organic phase, $LK_{(o)}^+$ is the ligand–cation complex, and "o" and "w" refer to the organic and water phases, respectively. The mechanism of the reaction has been widely studied [25].

A linear relationship between the peak current density and the square root of the polarization rate has been previously observed at constant concentrations of K$^+$ and ligand, which indicates that the phase-transfer reaction is diffusion controlled [26]. Mass transport of the cation is dependent on the ionophore concentration because it is present at a lower value than K$^+$. The diffusion coefficient is calculated from these data using the equation:

$$i_p = 2.69 \times 10^5 n^{3/2} A c \nu^{1/2} D^{1/2} \tag{4}$$

where *n* is the number of charges transferred, *A* is the interfacial area between the two immiscible liquids, *c* is the concentration of the electroactive species, υ is the polarization rate, and *D* is the diffusion coefficient. A value of $D_{K^+}^w$ = 5.0 x10^{-5} cm s^{-1} is calculated which is similar to the published value [12, 26]. The facilitated transfer of K$^+$ by the DB18C6 ionophore has been studied previously, and its phase-transfer mechanism across the ITIES interface is known. Therefore, it is a suitable reference for understanding the behavior of BPA in the water |1,2-DCE system.

3.2 BPA effects on the facilitated transfer of K$^+$

Figure 3 shows the cyclic voltammetric response for the facilitated transfer of K$^+$ by DB18C6 at the water |1,2-DCE interface in absence (solid line) and presence of BPA. The addition of BPA to the organic phase affects the peak current of K$^+$ transfer. The peak current decreases with increasing BPA concentration, because BPA absorbs at the interface due to its hydrophobic character as reflected in the value log K$_{ow}$ = 3.4 [27]. In fact, it does not transfer as charge species at pH = 6.8 since its p*K*a = 9.73 [28]. The observed behavior depends on the active area between the two liquids. Increasing concentrations of BPA collect at the interface, reduce the area available for ion transfer, and limit the charge-transfer current of potassium ion.

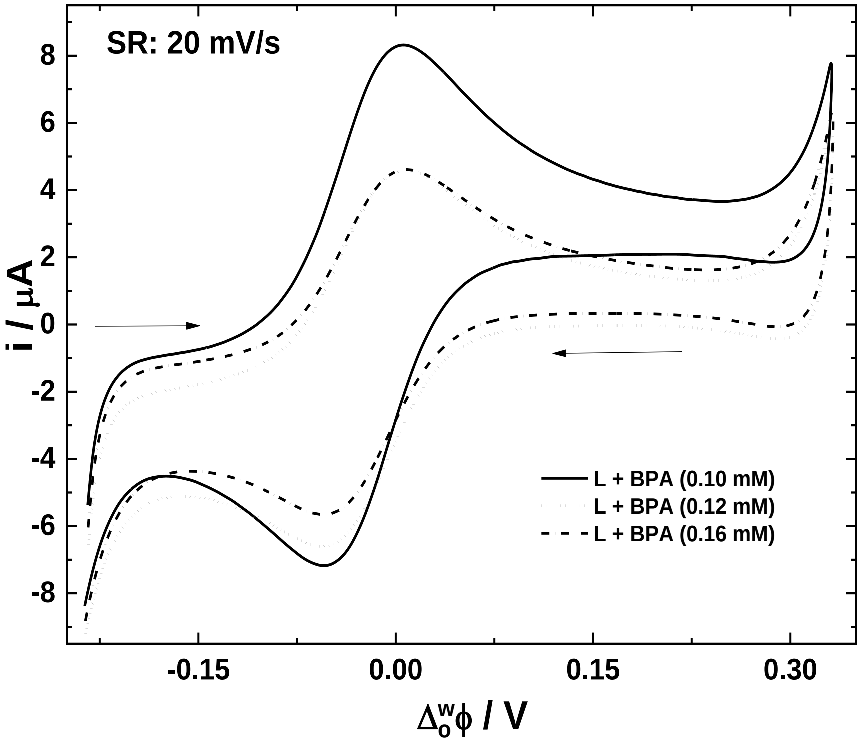

Figure 3. CV of the facilitated transfer of K^+ by the DB18C6 (0.14 mM) in presence of different concentrations of BPA. L= DB18C6.

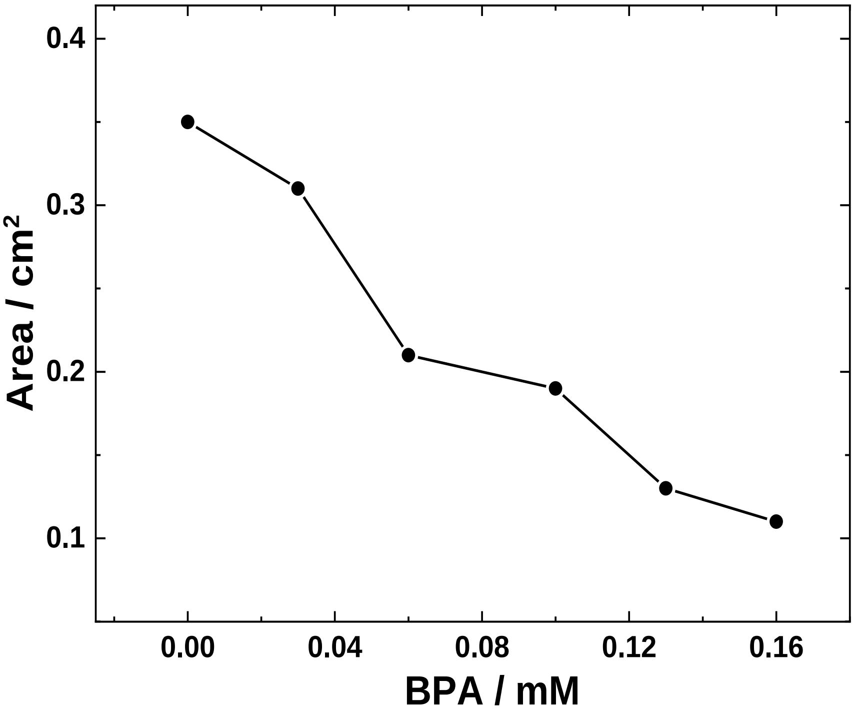

Figure 4. Active interfacial area in presence of different concentrations of BPA at the ITIES system.

The active area is estimated by use of the equation (4) and a diffusion coefficient of $D_{K^+}^{w}$ = 5.0 x10^{-5} cm s^{-1} for the DB18C6-facilitated transfer of K^+ in the absence of BPA. Figure 4 shows how the area changes as a function of BPA concentration. The idea of this compound is absorbing in the interface can be explained as the orientation adopted by BPA at the interface is one in which its two –OH groups extend into the aqueous solution while the hydrocarbon framework of the molecule remains in the organic phase. This explain that the current peak in the CV does no shift and it remains in the same potential and just the current intensity decrease in presence of the BPA. In VC the transfer of BPA is not observed in the potential range studied.

Figure 5 shows the square wave voltammetric response for the facilitated transfer of K^+ by DB18C6 in the presence of BPA. The square wave current decreases as the concentration of BPA in the organic phase increases. The potential of the square wave signal remains unchanged over the range of BPA concentrations examined. The result is similar to that obtained by cyclic voltammetry. Here, the current peak corresponds to a half-wave potential of $\Delta_o^w \phi_{1/2} = -0.022\ V$ for the facilitated transfer of K^+ at the water |1,2-DCE interface. The BPA blocks K^+ transfer by collecting at the interface and reducing the active area as its concentration in the organic phase increases.

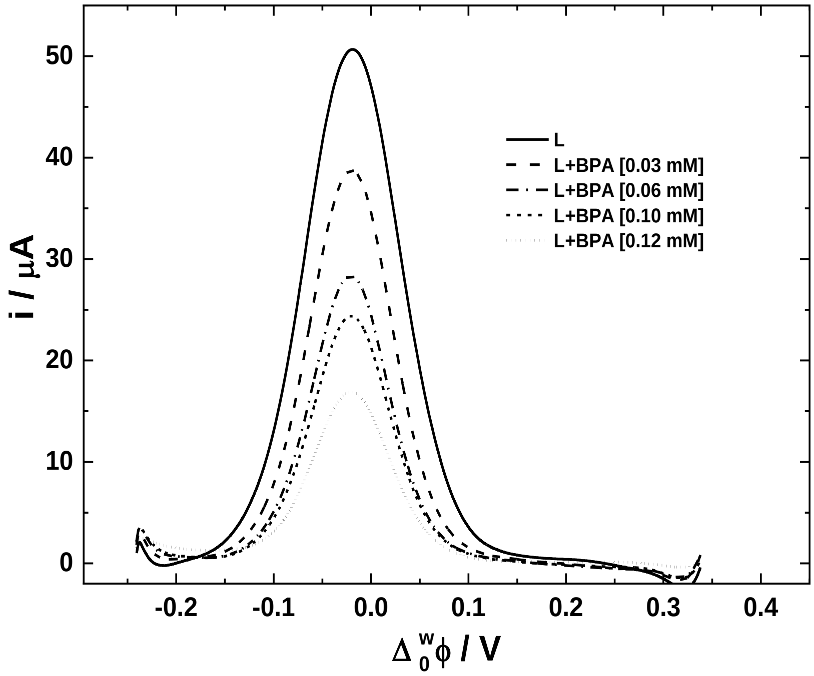

Figure 5. SWV for the facilitated transfer of K^+ by the L = DB18C6 at different concentrations of BPA. Esw(pulse) = 30 mV and 10 Hz of frequency.

3.3 Electrochemical impedance spectroscopy

Figure 6 displays the impedance spectrum (Nyquist diagram) for the facilitated transfer of K^+ by DB18C6 in the presence of BPA. The large resistance at high frequencies is attributed to the presence of the organic solvent. The system exhibits pseudo-capacitive behavior because the interface does not behave as an ideal capacitor. In an ideal system, the combination of pseudo-capacitance and charge-transfer resistance typically results in a semicircle at high frequencies. A semicircle is not observed here, because the charge transfer appears to be very fast. However, it is evident that the system is dominated by finite-layer diffusion at low frequencies. This is indicated by the linear response with a slope of approximately 1, which is consistent with diffusion-limited mass transfer behavior.

The impedance spectra shift slightly to the left as the concentration of BPA increases in the organic phase. The displacement indicates a decrease in solution resistance. However, an increase in impedance values is observed at low frequencies, which indicates an increase in the resistance to mass transfer through the interface. This behavior is interpreted in terms of an equivalent circuit model.

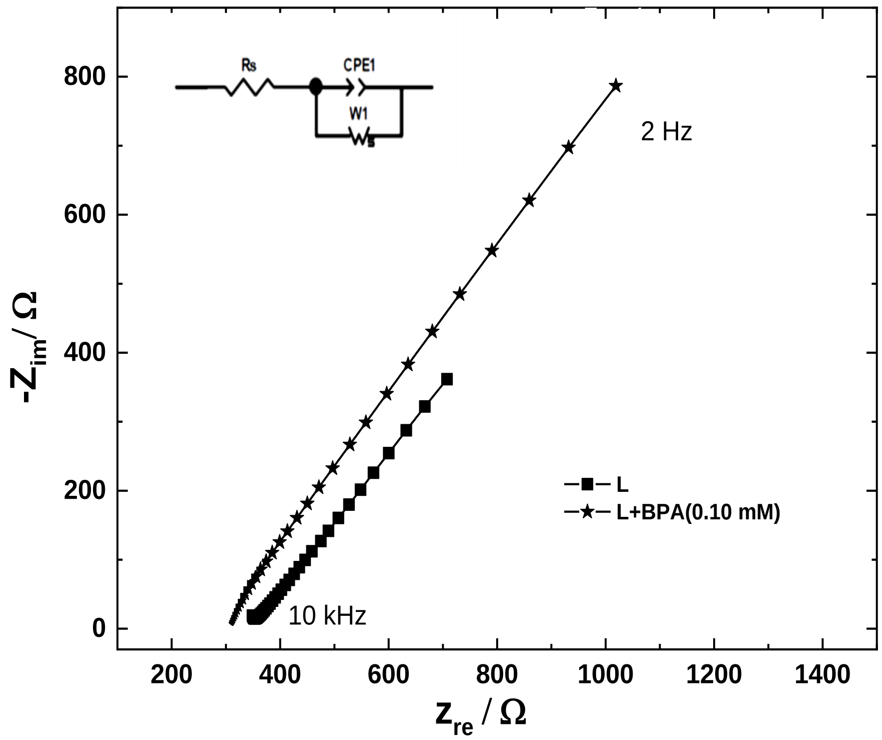

Figure 6. Nyquist diagram for the facilitated transfer of K^+ by the DB18C6 in presence of BPA at the ITIES system.

The impedance spectra were analyzed with the ZView2 program and the equivalent circuit in the inset of Figure 6. Table 1 summarizes the results, where it is observed that the solution resistance, R_S, decreases as the concentration of BPA increases. The constant phase element, CPE, is on the order of 10^{-6} and does not vary significantly. Values range between 0.94 and 1, which indicates that the system capacitance is not ideal, except at the higher BPA concentrations, where CPE $\approx$ 1.

Table 1. Parameters calculated according to the equivalent circuit (inset in figure 7) for the facilitated transfer of K^+ by the DB18C6 (L) at the water|1,2-DCE interface in presence of BPA.

	R_s	% Error	CPE	% Error	α	% Error	R_{difu}	% Error
L	402.3	0.27	$7.80x10^{-6}$	11.81	0.94	1.5	21741	25.49
L+BPA [0.03 mM]	337.5	0.22	$7.16\ x10^{-6}$	7.09	0.97	0.9	30367	24.26
L+BPA [0.06 mM]	335.5	0.20	$7.13\ x10^{-6}$	6.50	0.97	0.83	32315	23.23
L+BPA [0.09 mM]	349.4	0.21	$7.40\ x10^{-6}$	6.88	0.96	0.88	34100	26.40
L+BPA [0.12 mM]	251.5	0.17	$5.84\ x10^{-6}$	4.19	1.00	0.52	30914	13.20

R_s = solution resistance; CPE = phase constant element; R_{difu} = diffusion resistance; α = the exponent of the constant phase element.

Figure 7 shows the relationship between the diffusion resistance, R_{difu}, and the BPA concentration. The plot was constructed with the simulated data shown in Table 1. R_{difu} increases as the concentration of BPA increases. This behavior indicates that the interface is affected by the presence of BPA as observed in the CV and SWV experiments.

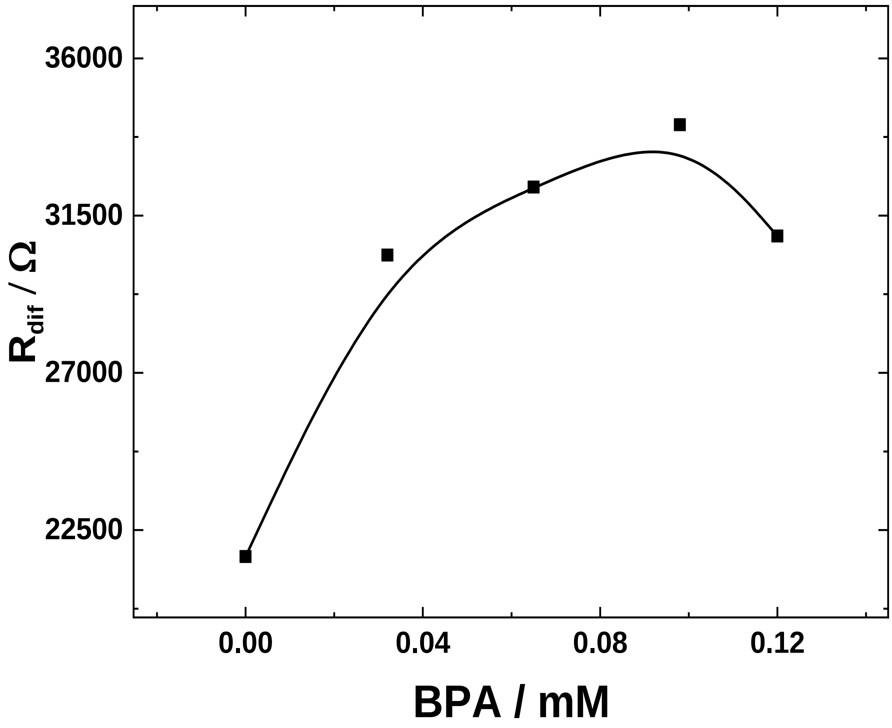

Figure 7. R_{difu} for the facilitate transfer of the K^+ by DB18C6 in presence of BPA at the water|1,2-DCE interface.

The impedance spectra of facilitated interfacial K^+ transfer is treated in terms of a finite diffusion-layer model. Kinetic parameters are evaluated by the method of Randles, which describes the relationship between the real and imaginary components of impedance and frequency as r_s = Z´ y 1/□c_s = Z´´.

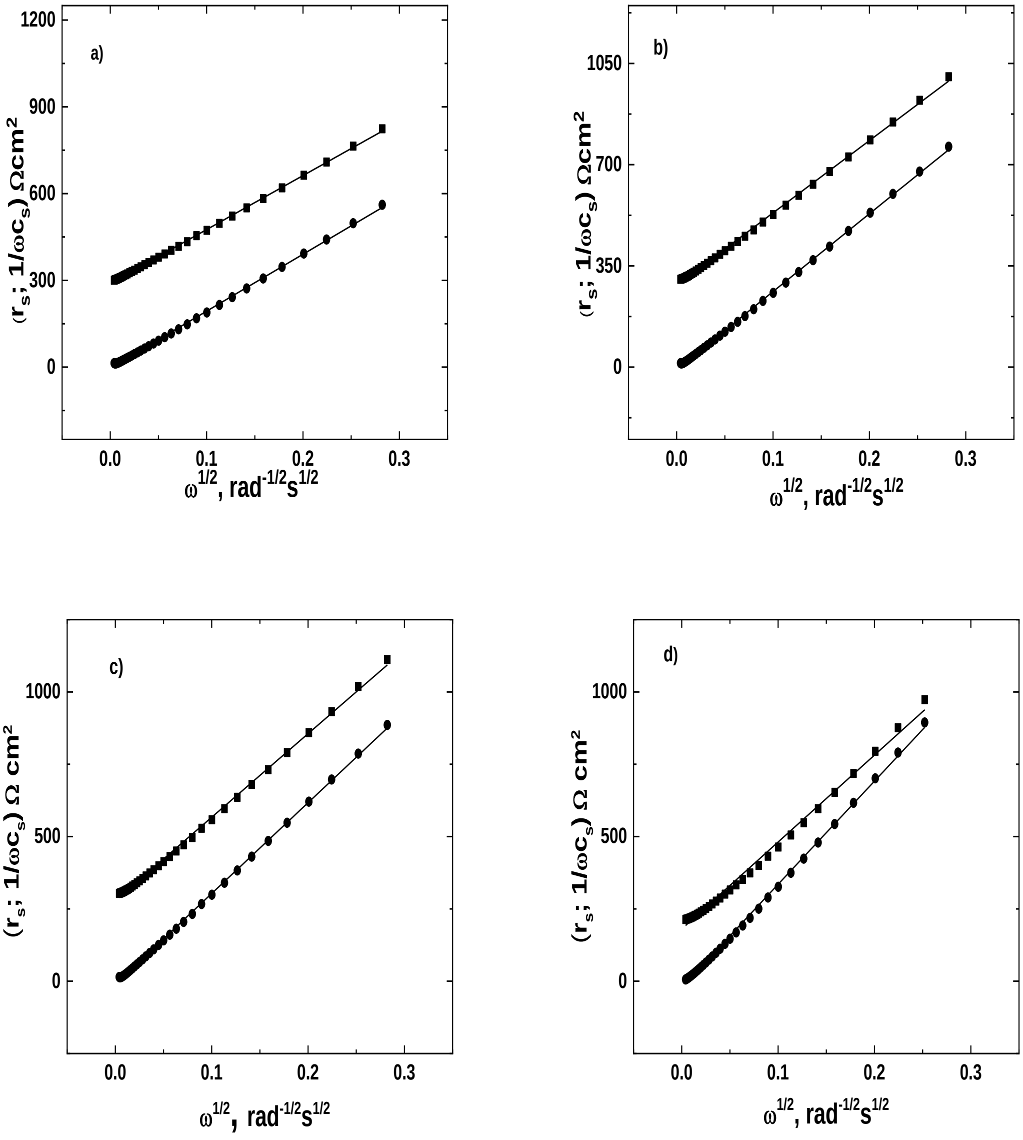

Figure 8. Dependence of the real and imaginary components for the facilitate transfer of the K^+ by DB18C6 (0.10 mM) in presence of BPA (a) 0.03, (b) 0.06, (c) 0.1 and (d) 0.12 mM at the water|1,2-DCE interface.

In this expression, r_s is the series resistance, Z′ is real component of the impedance, Z″ is the imaginary component of the impedance, $\omega = 2\pi f$ is the angular frequency, f is the frequency in Hz, and c_s is the pseudocapacitance. These quantities are related to the parameters of the faradaic process by the following equations [29]:

$$r_s=R_{\mathrm{CT}}+\sigma\omega-^{1/2} \tag{5}$$

$$1/\omega c_s=\sigma/\sqrt{\omega} \tag{6}$$

where R_{CT} is the charge transfer resistance and σ is the Warburg coefficient, which depends on the diffusion of ligand–K^+ complex and R_{CT}. Figure 8 shows the relationship predicted by equations (5) and (6).

The quantity σ was evaluated by fitting the data in Figure 8 over all concentrations of BPA. The diffusion coefficient of the ligand–K^+ complex in the organic phase, $D_{\mathrm{LK+}}$, determined using the previously estimated active area, was calculated from the following equation [30]:

$$\sigma=\frac{\mathrm{RT}}{\sqrt{2}z^2F^2A\left(D_{\mathrm{LM}^+}\right)^{1/2}c_L}\frac{(1+\rho)^2}{\rho} \tag{7}$$

where ρ = exp[F($\Delta_{\mathrm{o}}^{\mathrm{w}}\phi-\Delta_{\mathrm{o}}^{\mathrm{w}}\phi_{1/2}$)/RT], *A* is the active area between the two liquids, and c_L is the ligand concentration. $\Delta_0^{\mathrm{w}}\phi$ and $\Delta_{\mathrm{o}}^{\mathrm{w}}\phi_{1/2}$ are the Galvani potential and half-wave potential, respectively, at the water|1,2-DCE interface. $D_{\mathrm{LK+}}$ values in cm^2 s^{-1} at various BPA concentrations (*x* mM) are: 1.37 x10^{-5} (0) 6.1 x 10^{-6} (0.03), 9.6 x 10^{-6} (0.06), 1.08 x 10^{-5} (0.10) and 1.5 x 10^{-5} (0.12). The diffusion coefficient remains effectively constant on the order of 10^{-5} and is close to the value of $D_{\mathrm{LK+}}$ in the absence of BPA obtained by CV.

4. CONCLUSIONS

This work examines the influence of BPA on the facilitated transfer of K^+ by DB18C6 using CV and EIS. The hydrophobic BPA molecule does not partition into the aqueous phase in the range of the potential window studied, however the effect of this latter induce that the BPA absorbs at the organic|aqueous interface, where it reduces the active area between the two immiscible liquids. The absorption impedes the facilitated transfer of K^+ by the DB18C6 ligand. Electrochemical impedance analysis shows that increasing concentrations of BPA decreases the resistance of the solution, which accords with the results of CV experiments. The diffusion coefficient of the $K(D18C6)^+$ complex remains nearly equal to its value in the absence of BPA.

ACKNOWLEDGMENTS
EMH thanks CONACyT for the scholarship granted for postgraduate studies (grant No. 878874) at the UAdeC.

References

1. J. Guo, Y. Yuan, and S. Amemiya, *Anal. Chem.*, 77 (2005) 5711.

2. P. Jing, Y. Kim, and S. Amemiya, *Langmuir*, 25 (2009) 13653.
3. A. Trojánek, J. Langmaier, E. Samcová, and Z. Samec, *J. Electroanal. Chem.*, 603 (2007) 235.
4. G. Herzog, V. Kam, and D. W. M. Arrigan, *Electrochim. Acta*, 53 (2008) 7204.
5. F. Kivlehan, Y. H. Lanyon, and D. W. M. Arrigan, *Langmuir*, 24 (2008) 9876.
6. V. Beni, M. Ghita, and D. W. M. Arrigan, in *Biosensors and Bioelectronics*, Elsevier Ltd 20 (2005) 2097.
7. G. Herzog , B. McMahon, M. Lefoix, N.D. Mullins, C.J. Collins, H.A. Moynihan and D.W.M. Arrigan, *J. Electroanal. Chem.*, 622 (2008) 109.
8. A. Berduque, R. Zazpe, and D. W. M. Arrigan, *Anal. Chim. Acta*, 611 (2008) 156.
9. Y. Yuan and Y. Shao, *J. Phys. Chem. B*, 106 (2002) 7809.
10. J. Koryta, *Electrochim. Acta*, 24 (1979) 293.
11. F. Li, Y. Chen, M. Zhang, P. Jing, Z. Gao and Y. Shao, *J. Electroanal. Chem.*, 579 (2005) 89.
12. P. D. Beattie, A. Delay, and H. H. Girault, *Electrochim. Acta*, 40 (1995) 2961.
13. J. A. Ribeiro, F. Silva, and C. M. Pereira, *Talanta*, 88 (2012) 54.
14. X. Huang, L. Xie, X. Lin, and B. Su, *Anal. Chem.*, 89 (2017) 945.
15. T. Iwai, M. Kramaric, D. Crabbe, Y. Wei, R. Chen, and M. Shen, *Anal. Chem.,* 90 (5) (2018) 3067.
16. M. L. Colombo, J. V. Sweedler and M. Shen,. *Anal. Chem.* 87 (10) (2015) 5095.
17. C. J. Collins, C. Lyons, J. Strutwolf, and D. W. M. Arrigan, *Talanta*, 80 (2010) 1993.
18. M. C. Martins, C.M. Pereira, H.A. Santos, R. Dabirian, F. Silva, V. García-Morales and J.A. Manzanares, *J. Electroanal. Chem.*, 599 (2007) 367.
19. H. A. Santos, C. M. Pereira, and F. Silva, *Port. Electrochim. Acta*, 22 (2005) 263.
20. A. G. Reyes-Reyes, J. Amador-Hernández, and M. Velázquez-Manzanares, *J. Mex. Chem. Soc.*, 58 (2014) 326.
21. R. C. Burgos-Castillo, I. Sirés, M. Sillanpää, and E. Brillas, *Chemosphere*, 194 (2018) 812.
22. M. Česen, K. Lenarčič, V. Mislej, M. Levstek, A. Kovačič, B. Cimrmančič, N. Uranjek, T. Kosjek, D. Heath, M.S. Dolenc and E. Heath, *Sci. Total Environ.*, 616–617, (2018) 752.
23. A. Careghini, A. F. Mastorgio, S. Saponaro, and E. Sezenna, *Environ. Sci. Pollut. Res.*, 22 (2015) 5711.
24. A. Sabela, V. Marecek, Z. Samec and R. Fuocot, *Electrochim. Acta*, 37(2), (1992) 231.
25. P. D. Beattie, R. G. Wellington, and H. H. Girault, *J. Electroanal. Chem.*, 396 (1995) 317.
26. E. Martínez Hernández, J. Amador-Hernández, R. Antaño López, E. M. Colunga Urbina , I.M. de la Garza Rodríguez and M. Velázquez-Manzanares. *ECS Transactions*, 94 (1) (2019) 125.
27. C. P. Groshart, P. C. Okkerman, and A. M. C. M. Pijnenburg, *Minist. van Verkeer en Waterstaat*, (2001) 1.
28. H. Sambe, K. Hoshina, K. Hosoya and J. Haginaka, *J. Chromatogra., A* 1134 (2006) 16.
29. Y. Cheng and D. J. Schiffrin, *J. Chem. Soc. Faraday Trans.*, 89 (1993) 199.
30. T. Osakai, T. Kakutani, and M. Senda, *Bull. Chem. Soc. Jpn.*, 57 (1984) 370.