

Kinetics of Heavy Metal Extraction by Diazadibenzo Crown Ethers at the Water/ 1,2-Dichloroethane Interface. Electrochemical Study.

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Received: 2 February 2022 / Accepted: 19 March 2022 / Published: 5 April 2022

In this study, the kinetics of the facilitated transfer of Pb^{2+} , Cd^{2+} , and Zn^{2+} by a new diazadibenzo crown ether (DB, diazadibenzo-18-crown-6, diazadi (t-butylbenzo)-18-crown-6, and diazadibenzo-15-crown-5) across the water|1,2-dichloroethane interface was studied using cyclic voltammetry (CV) and electrochemical impedance spectroscopy. The experiments were performed using a two-electrode cell configuration. The electrochemical impedance spectroscopy results showed that the values for the rate constant were in the order of $10^{-3} \text{ cm s}^{-1}$, depending on the metal in combination with the ligand structure. The experiments made it possible to understand the ionophoretic ability of the DB ligands to transport ionic metals across the water|1,2-dichloroethane interface. The chemical structure of the DB plays an important role in ion selectivity and kinetic values. This study contributes toward a better understanding of the transfer of heavy metals within biological cells.

Keywords: Heavy metals, ITIES, EIS, diazadibenzo crown ethers

1. INTRODUCTION

Recently, mechanisms that regulate the processes of extraction of heavy metals from contaminated aqueous effluents, and the partitioning of ionic species across biological barriers has become the focus of considerable research attention. Studies on the interfaces between two immiscible electrolyte solutions (ITIES) can be used to understand this phenomenon. In fact, the ITIES can be useful in diverse disciplines, such as in chemistry, biochemistry, or biology.

Over 40 years ago, Koryta proposed assisted ion transfer at the ITIES using dibenzo-18-crown-6 (DB18C6) and the ionophore *valinomycin* [1]. Since then, metal transfer facilitated by ionophores across ITIES has been widely studied [2]. The function of ionophores is to minimize the energy requirements of free metal transfer through the water–organic solvent interface, as it will require a large amount of energy for the cations to transfer itself. Through these studies, it has been possible to understand ion transfer across hydrophobic barriers, such as the selective extraction of metal ions across biphasic systems, among others [3, 4].

Studying the behavior of heavy metals in biological systems is important because of the serious damage they cause to living beings. However, *in vivo* studies in biological systems require specialized infrastructure and control parameters such as pH and ionic strength, which are complicated to establish.

In literature, there are some examples of studies on ITIES that deal with facilitated ion transfer, such as the extraction of Ni^{2+} , Cd^{2+} , and Cu^{2+} facilitated by 2,2':6',2''-terpyridine at the water|2-heptanone interface [5]. The transfer of Al^{3+} , facilitated by the prometryn herbicide at the water |1,2-dichloroethane interface has also been studied [6]. Other divalent metal ion transfers at the ITIES such as the transfer of Cd^{2+} facilitated by 1,10-phenanthroline at the micro-interface has also been considered [7]. Another compound that has been used as a ligand to transport metal ions at the ITIES is the 4-morpholinoacetophenona-4-ethyl-3-thiosemicarbazone at the water|1,2-dichloroethane interface [8]. Lager *et al.* (1998) used a series of highly hydrophobic thioether ligands to extract heavy metal ions at the water|1,2-dichloroethane interface [9]. The ITIES investigation has been extended to micro-interfaces (microITIES). From an analytical point of view, studies on the ability of 8-hydroxyquinoline to quantify metal ions such as Pb^{2+} , Cd^{2+} , and Zn^{2+} using microITIES have been performed [10].

In this field, there have been extensive studies on the selectivity of the ligand at the ITIES. However, only a few studies have focused on the kinetics of metal ion transfer at the liquid–liquid interface, and most of these studies were performed using a supported liquid membrane (SLM), for example, the facilitated transport of Cd^{2+} using cyanex 923 as the ionophore [11], or the transfer of Cu^{2+} using calix [4] and arene [12]. In these studies, the ligand's ability to transfer metal ions at the SLM was assessed using parameters such as co-anions, pH, and carrier concentration.

The kinetics of monovalent ions have also been evaluated from water to the organic phase, assisted by DB18C6 at the interface between the two liquids, and the apparent rate constant and transfer coefficient were determined [13]. The effect of a phospholipid monolayer on the kinetics of IrCl_6^{2-} transfer across the water|1,2-dichloroethane interface has also been studied [14]. Other studies, including the kinetics of TEA^+ at the water|1,2-dichloroethane (DCE) interface, were performed through steady-state voltammetry at nano-ITIES [15]. From an analytical point of view, the detection of chemical compounds of biological interest such as neurotransmitters and neuromodulators by nano-ITIES [16] and γ -aminobutyric acid detection with a nano-ITIES pipet electrode at the water|1,2-DCE-octanoic acid interface has been carried out [17]. Additionally, studies on the adsorption and ionophoretic activities of proteins at the ITIES have recently been carried out [18].

Studies on the transfer of ions provided by ionophores through ITIES have facilitated the generation of models to explain the ion transfer phenomena of essential metals, including heavy metals, across biological or artificial membranes (selective extraction models). The aim of this study was to

investigate the kinetics of the transfer of heavy metal ions provided by the ionophore family of diazadibenzo crown ethers through the water|1,2-dichloroethane (1,2-DCE) interface.

2. EXPERIMENTAL

For electrochemical experiments, a two-electrode cell configuration was employed. Two Ag/AgCl electrodes with a large area (7.0 cm²) and a planar interface were easily adjusted in the cell using a syringe.

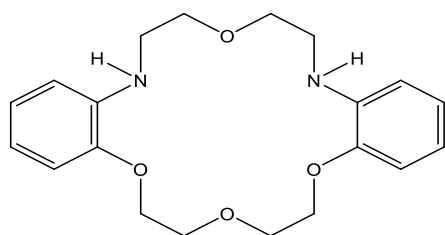
Tetraphenylarsonium chloride (TPAsCl, Fluka), 1,2-DCE (Gold Label, Aldrich), and potassium tetrakis (4-chlorophenyl)borate (KTPBCl, Fluka purum) were used as received. Tetraphenylarsonium tetrakis(4-chlorophenyl)borate (TPAsTPBCl) was precipitated from the corresponding chemicals and recrystallized twice from acetone (BDH, AnalaR). The ligands were diazadibenzo crown ethers (DB) (Fig. 1) and it was a gift from Dr. J.C. Aguilar of the UNAM. The preparation and characterization details can be found in reference [19]. PbCl₂, ZnCl₂, and CdCl₂ (Sigma-Aldrich) were employed as supporting electrolytes in the aqueous phase. Aqueous solutions were prepared in deionized water (Jalmek). All experiments were carried out at 25 ± 1 °C. During the measurements, the electrochemical cell was placed inside a Faraday cage.

CV and electrochemical impedance spectroscopy (EIS) were carried out using a potentiostat/galvanostat PGSTAT30 (Autolab, Eco Chemie). EIS was performed with a sinusoidal signal of 10 mV for different imposed potentials; no IR compensation was used. Finally, the spectral signal was recorded at frequencies in the range 1 – 1000 Hz. The solution resistance was extrapolated at a high frequency in the impedance plot. Additionally, the impedance spectra were processed with Microcal Origin 6.0 (Microcal Software Inc.).

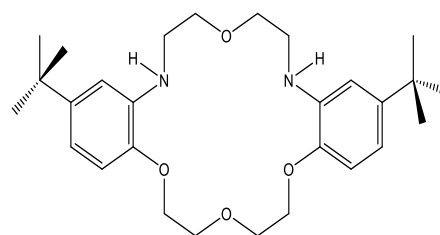
The measured potential corresponds to the following cell:



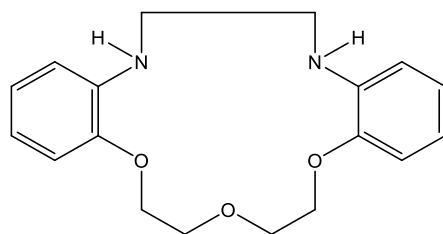
where x is the ionophore concentration in the organic phase, y is the metal concentration in the aqueous phase, σ represents the interface of the study, and Ag|AgCl₁ and Ag|AgCl₂ are reference electrodes.



Diazadibenzo-18-Crown-6 (L1)



Diazadi(t-butylbenzo)-18-crown 6 (L2)



Diazadibenzo-15-crown-5 (L3)

Figure 1. Chemical structure of dibenzo crown ethers.

The potentials were reported on the Galvani potential scale and calculated according to the following equation:

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

where $\Delta_o^w \phi$ is the Galvani interfacial potential, and $\Delta_o^w \phi_{TPAs^+}$ is the Galvani potential at the reference interface, expressed as follows:

$$\Delta_o^w \phi_{TPAs^+} = \Delta_o^w \phi_{TPAs^+}^o + \frac{RT}{zF} \ln \frac{a_{TPAs^+}^o}{a_{TPAs^+}^w} \quad (2)$$

The standard transfer potential for $TPAs^+$ ($\Delta_o^w \phi_{TPAs^+}^o$), was set to -0.364 V [20].

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetry

Figure 2a shows the cyclic voltammogram for facilitated Pb^{2+} transfer by L2 at the water|1-2 DCE interface using a two-electrode cell. The half-wave potential for the process is similar to that obtained in a four-electrode cell [4]. As observed in the figure, the peak-to-peak difference was 60 mV, which is close to the theoretical value (59 mV) described by the Nernst equation, and is a reversible behavior for the metal extraction. Using a two-electrode cell configuration can eliminate the Luggin capillaries, which are common in the four-electrode cell, where they cause a geometric effect due to the deviation of the electric field. It is easier to extract the impedance signal when a two-electrode cell is employed, compared to when a four-electrode cell is employed. Additionally, the interface can be easily adjusted to a flat interface between the two immiscible liquids instead of having a typical meniscus [21].

In addition, voltammetry experiments were carried out for other cations and ionophores L1, L2, and L3. Figure 2b and 2c show the transfer of Cd^{2+} and Zn^{2+} facilitated by L2 at the water|1,2-DCE interface, indicating a reversible wave transfer current. The transfer of these cations takes place at the edge of the potential window, specifically in the positive region, meaning that this process requires more energy to facilitate the transport of Cd^{2+} and Zn^{2+} compared to the transfer of Pb^{2+} by L2 (for example). A similar behavior was observed when L1 and L3 were used as ligands. The electrochemical behavior of the Pb^{2+} transfer can be explained by the fact that Pb^{2+} has a higher ionic radius (1.18 Å) compared to

that of Zn^{2+} (0.75 Å) and Cd^{2+} (0.95 Å); moreover, because of the weak hydration sphere, the ionophores can form a stable complex with Pb^{2+} rather than Zn^{2+} and Cd^{2+} .

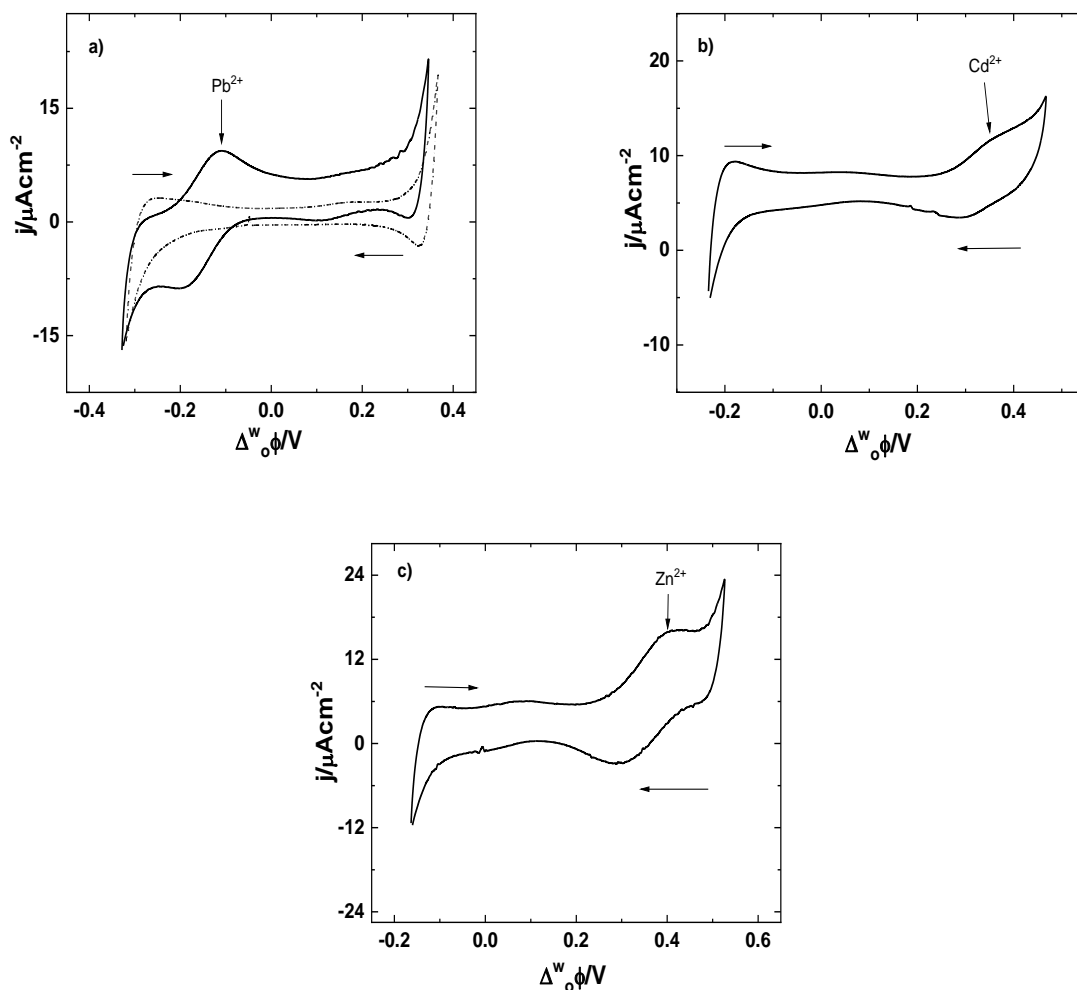


Figure 2. Facilitated transfer of (a) Pb^{2+} (PbCl_2 0.01 M), (b) Cd^{2+} (CdCl_2 0.01 M) and (c) Zn^{2+} (ZnCl_2 0.01 M) by L2 (0.10 mM) across the water|1,2-DCE interface (solid line). Supporting electrolyte: TPAStPBCl 0.01 M in the organic phase and 0.01 M metallic salt in the aqueous phase (dotted line). Sweep rate: 20 mV s^{-1} .

3.2 Kinetics of metal extraction

According to the impedance measurements at the ITIES, a high solution resistance was observed owing to the presence of the organic solvent, a phenomenon that is common in the ITIES system. In fact, the solution resistance dominated the signals at higher frequencies.

Figure 3 shows the impedance spectra signal (Nyquist diagram) for the transfer of Pb^{2+} , Cd^{2+} , and Zn^{2+} by ionophore L2. As observed, the impedance signal for the base electrolyte is higher than the signal observed when the ionophore is present in the organic phase. The decrease in the impedance signal

in the presence of the ligand indicates that a faradaic reaction occurs, which means that there is a transfer of the metal across the interface, as observed during the CV experiments.

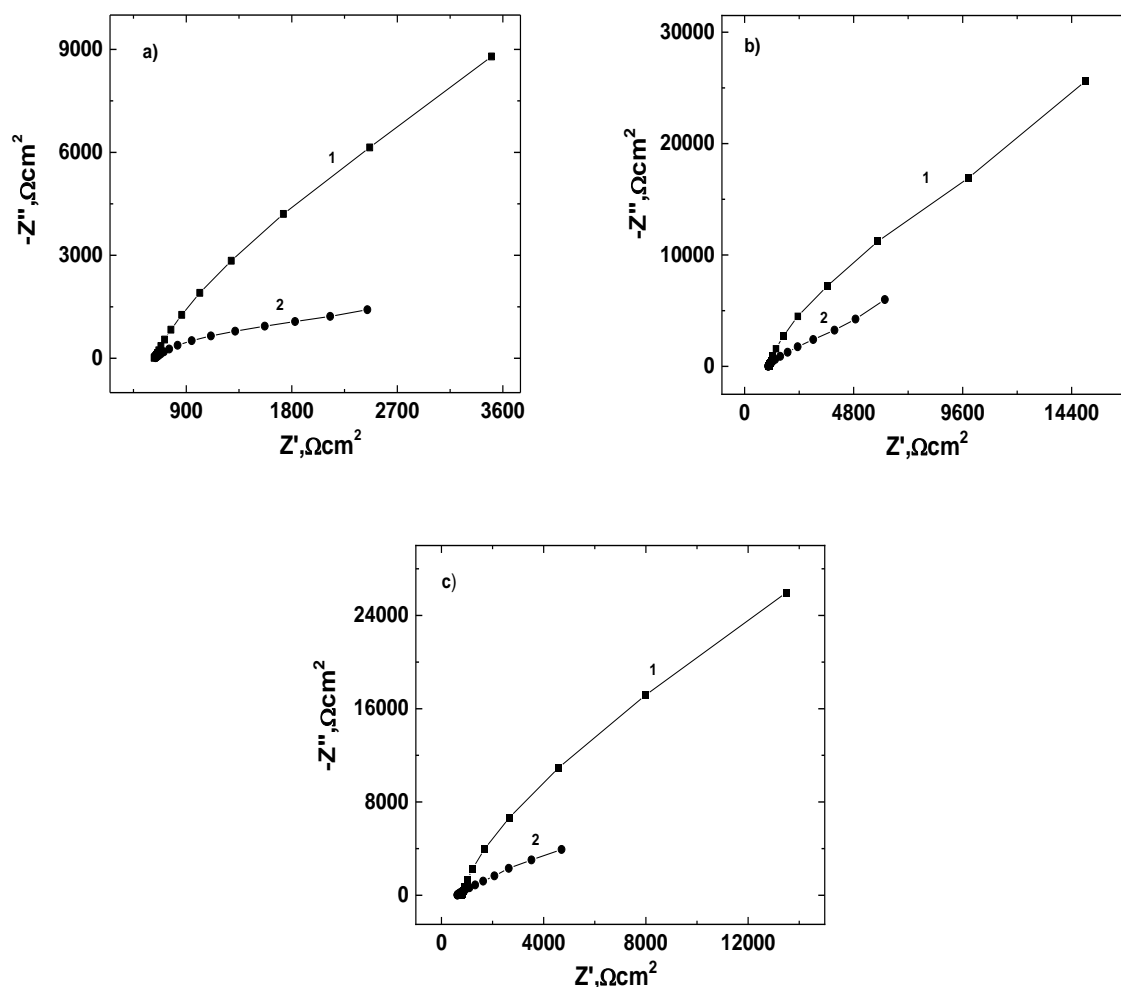


Figure 3. Nyquist diagram for the facilitated transfer of a) Pb^{2+} , b) Cd^{2+} and c) Zn^{2+} by L2 at the water|1,2-DCE interface. In the absence of the ligand (1) and in presence of the ligand (2) at the half-wave potential.

The impedance spectra signal was measured every 10 mV within the potential region, where the metal transfer took place, as was observed in the CV. In fact, the potential to perform the EIS was close to the half-wave potential before and after the transfer. Figure 3 shows the impedance signal obtained at half-wave potential for the transfer of Pb^{2+} , Cd^{2+} , and Zn^{2+} facilitated by L2, whereas Figure 4 shows the facilitated transfer of Pb^{2+} , Cd^{2+} and Zn^{2+} by ionophore L3, with an impedance plot that clearly follows a pattern that is similar for all the tested ligands and cations. It is notable that the impedance signal for the supporting electrolyte contained a capacitive current, as shown in CV. This current had some influence on the impedance measurement; hence, the admittance for the support electrolyte signal was calculated and then subtracted from the admittance obtained for the facilitated metal ion transfer by the ionophore. Thus, the result was a faradaic reaction.

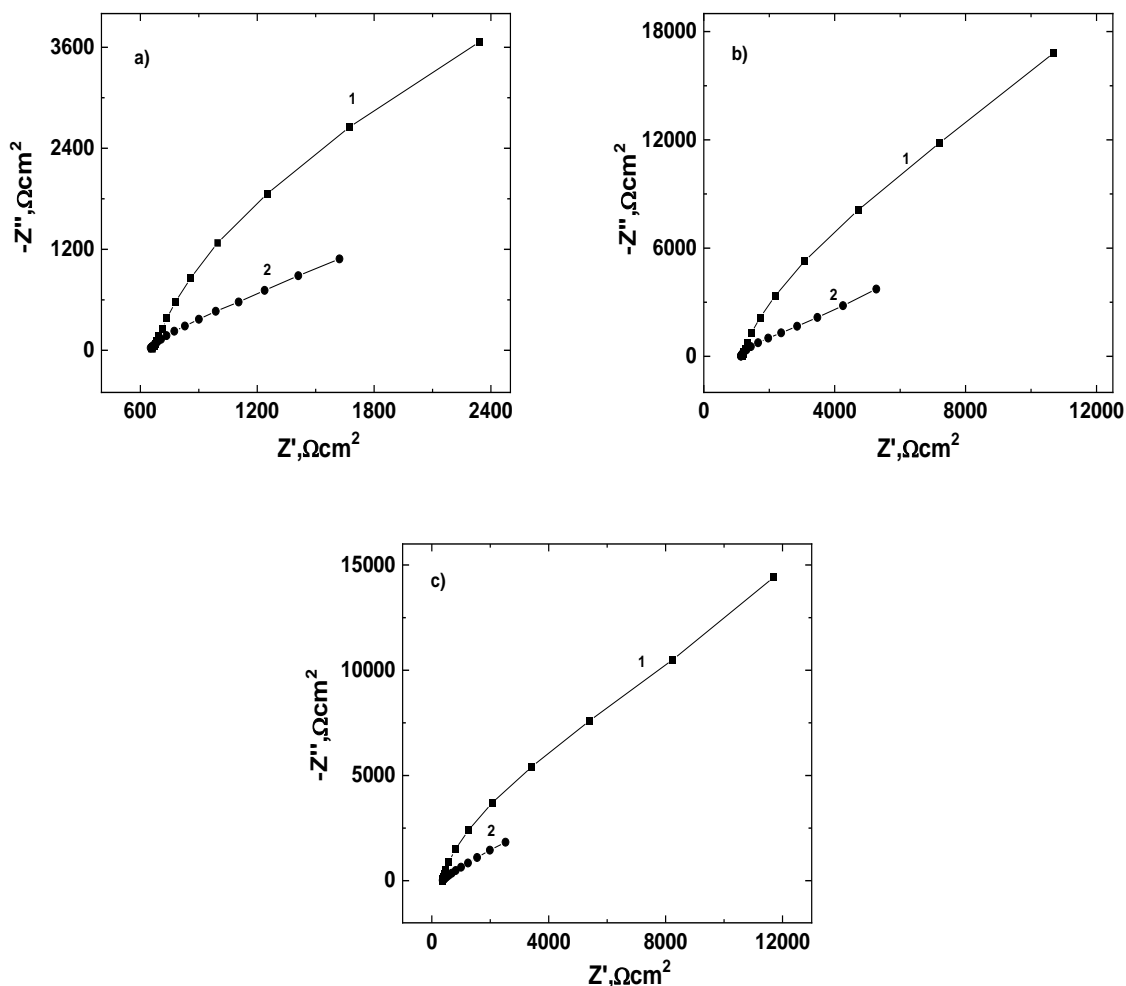


Figure 4. Nyquist diagram for the facilitated transfer of a) Pb^{2+} , b) Cd^{2+} and c) Zn^{2+} by L3 at the water|1,2-DCE interface. In the absence of the ligand (1) and in presence of the ligand (2) at the half-wave potential.

The kinetic parameters were evaluated following the Randles method, because this method allows for the expression of the real and imaginary components of the impedance spectra for the metal transfer. $r = Z$, $r_s = Z'$, $1/\omega c_s = Z''$ as a function of $\omega^{-1/2}$, where ω is the angular frequency ($\omega = 2\pi f$, f = frequency in Hz), and c_s is the capacitance related to the transfer process (Fig. 5) [21]:

$$r_s = R_{CT} + \sigma \omega^{-1/2} \quad (1)$$

$$1/\omega c_s = \sigma / \sqrt{\omega} \quad (2)$$

where σ is the Warburg coefficient, which depends on the diffusion of the metal, and R_{ct} is the charge transfer resistance.

Thus, σ can be defined as follows [22]:

$$\sigma = \frac{RT}{\sqrt{2}Z^2F^2A(D_{LM^+})^{1/2}c_A} \frac{(I+\rho)^2}{\rho} \quad (3)$$

where $\rho = \exp[F(\Delta_0^w\phi - \Delta_0^w\phi_{1/2})/RT]$, A is the interfacial area, c_A is the ligand concentration, and D_{LM^+} is the diffusion constant for the complex ionophore cation in the organic phase. $\Delta_0^w\phi$ and $\Delta_0^w\phi_{1/2}$ are the Galvani potential and half-wave Galvani potential across the water|1,2-DCE interface.

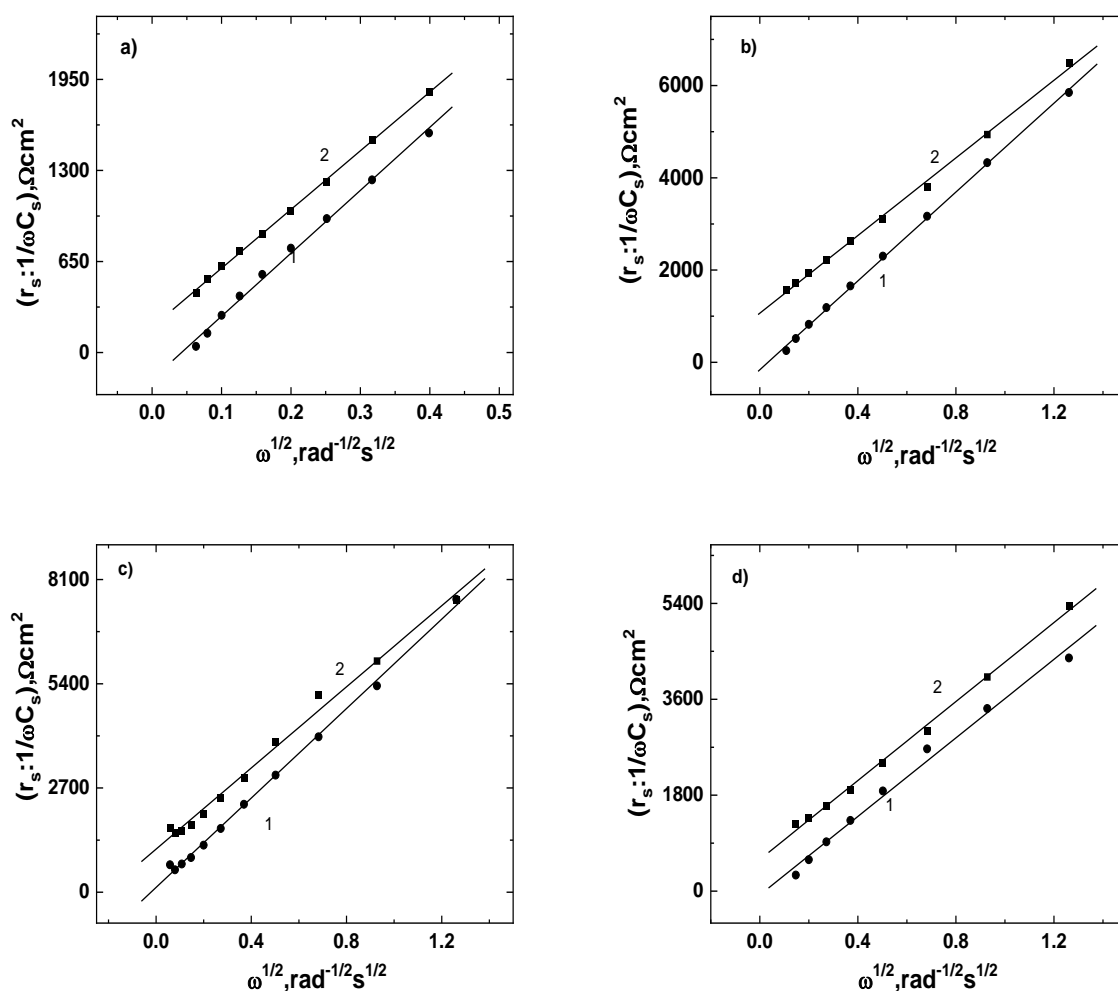


Figure 5. Dependence of imaginary (1) and real (2) components of the assisted metal transfer of a) Pb^{2+} , b) Cd^{2+} by L1 and c) Cd^{2+} , d) Zn^{2+} by L2 at the water|1,2-DCE interface on $\omega^{1/2}$ at the half-wave potential.

The kinetic values obtained from the experimental data are shown in Fig. 6. This representation has been previously discussed; thus, the data were adjusted to the following equation [23]:

$$\ln\left(\frac{\delta}{1 + \exp(-b)}\right) = \ln\left(\frac{k_s}{\sqrt{D_{LH^+}}}\right) + ab \quad (4)$$

where $\delta = (2\omega)^{1/2} / (\omega r_s c_s - 1)$, $b = zF (\Delta_o^w \phi - \Delta_o^w \phi_{1/2}) / RT$, k_s is the apparent rate constant, and α is the transfer coefficient.

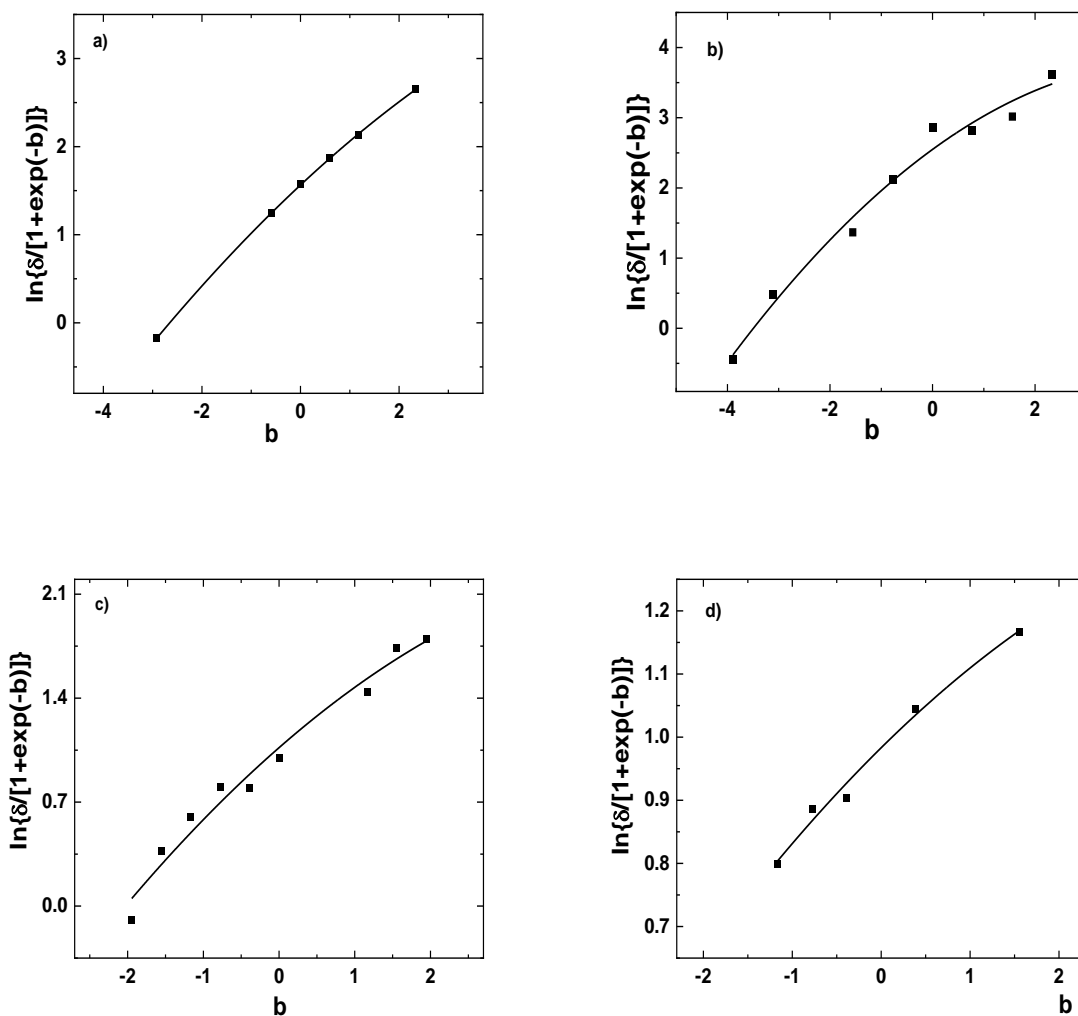


Figure 6. Dependence of $\ln\{\delta/[1+\exp(-b)]\}$ on the interfacial Galvani potential for the facilitated transfer of a) Pb^{2+} , b) Cd^{2+} and c) Zn^{2+} by L1 and d) Pb^{2+} by L2.

The k_s values were found to be similar for the facilitated (assisted) transfer of ionic metals by hydrophobic ionophores [12], whereas the transfer coefficient (α) for the majority of the metals and ligands tested revealed a reversible process. The latter can be explained by making an analogy; in the classical theory of electron transfer, α is related to the symmetry of the potential energy barrier, however, in ITIES it may be more related to the effects of the electrical double layer and the trend in the complex metal–ionophore, determined by phase. For a single ion transfer, a value of $k = 0.2 \text{ cm s}^{-1}$ was obtained for the transfer of TEA^+ at the liquid–liquid micro-interface supported at the tip of a microcapillary by steady-state voltammetry and EIS studies [24]; a more extensive discussion dealing with the kinetics for this cation is presented in ref [25]. The difference between our data and the latter, in addition to the size

of the interface, is that the single ion transfer is faster than the facilitated ion transfer in which the interfacial reaction between the cation and the ligand is probably the limiting process. In fact, Beattie *et al.*, (1995) studied the transfer kinetics of the potassium ion facilitated by BD18C6 through a micro-interface formed between a small hole made on a polymeric membrane and 1,2-DCE, and found a value of $k = 0.31 \text{ cm s}^{-1}$. This value was greater than the values presented in this study. The difference is probably because Beattie *et al.* employ a small area between the two liquids that minimizes the solution resistance and generates high kinetic constants [26]. However, the experimental setup is quite difficult to manipulate, especially when building an electrochemical cell. Table 1 summarizes the kinetic parameters obtained for the three tested ionophores at the water|1,2-DCE interface.

Table 1. Kinetic parameters for the facilitated transfer of metal ions by ionophores at the water|1,2-DCE interface.

Ionophore	Cation	k_s / cms^{-1}	α
L1	Pb^{2+}	9.0×10^{-3}	0.45 ± 0.08
	Cd^{2+}	1.8×10^{-2}	0.71 ± 0.01
	Zn^{2+}	4.6×10^{-3}	0.43 ± 0.08
L2	Pb^{2+}	5.5×10^{-3}	0.32 ± 0.09
	Cd^{2+}	4.9×10^{-3}	0.65 ± 0.09
	Zn^{2+}	4.6×10^{-3}	0.72 ± 0.05
L3	Pb^{2+}	5.8×10^{-3}	0.73 ± 0.24
	Cd^{2+}	4.3×10^{-3}	0.49 ± 0.09
	Zn^{2+}	5.4×10^{-2}	0.41 ± 0.04

By contrast, k_s is independent of the molecular volume of the ligand. In fact, L1 shows a higher kinetic value for the transfer of Pb^{2+} and Cd^{2+} compared to the extraction process with the other ligands. Despite the fact that the facilitated transfer of Zn^{2+} to the organic phase by L3 requires a large amount of energy, its rate constant is greater, indicating that this cation is transported across the interface.

Figure 7 shows the relationship between k_s and the function of the transfer coefficient. As observed in all the experiments, a reversible process occurred because the values of the transfer coefficient were close to 0.5, which is consistent with the signal observed during the CV experiments. However, for ionophore L3, a less reversible process was observed when Pb^{2+} was transported, probably due to the large ionic diameter of this cation. The other ionophores showed values close to 0.5 for the transport of Pb^{2+} .

The ionophores L1 and L2 only differ in the alkyl group present as substituent; L1 showed a transfer coefficient equal to 0.45, which is close to that for a reversible process and its k_s was the greatest compared to L2 and L3.

In the case of Cd^{2+} transfer, L1 showed a k_s value greater than that for L2 and L3. In fact, the α value was higher than that for L2 and L3. This probably explains why Cd^{2+} extraction was faster at the ITIES.

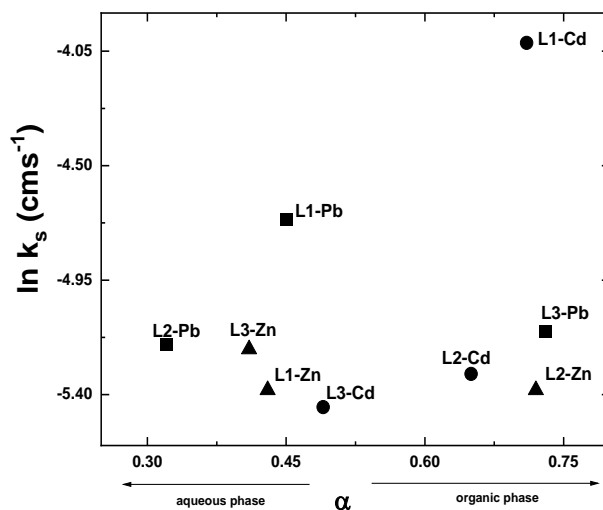


Figure 7. Relationship between k_s and α for the facilitated transfer of the metal ions by L1, L2 and L3 at the ITIES.

Finally, the transport of Zn^{2+} at the ITIES by the three ionophores showed similar k_s values for L1, L2, and L3. It is notable that the transfer coefficient can display certain tendencies during the transfer of metal ions at the ITIES, as shown in Figure 7. For example, the transfer of Zn^{2+} by L1 tends toward the aqueous phase, whereas for L3, it tends toward the organic phase.

4. CONCLUSION

It was shown that it is possible to study the facilitated transfer of heavy metals ions by DB at the liquid–liquid interface. The facilitated transfer potential for the three cations studied takes place in the middle of the potential window in the CV experiments. With this system, it was possible to study the kinetics for the facilitated transfer of certain cations at the water|1,2-DCE interface. The results showed that the chemical structure of the ligand and the chemical nature of the cation (atom radii) are the rate-determining factors. This study can be useful as a model for understanding the ion transfer that occurs within biological systems.

ACKNOWLEDGEMENTS

GGT thanks CONACyT for scholarship awarded for postgraduate studies at the Universidad del Mar, Oaxaca, Mex..

References

1. J. Koryta, *Electrochim. Acta*, 24 (1979) 293.
2. L., Tomaszewsky, G., Lager and H. H., Girault, *Anal. Chem.*, 71 (1999) 837.
3. F., Reymond, D., Fermín, H. J. Lee and H. H., Girault, *Electrochim. Acta*, 45 (2000) 2647.

4. M. Velázquez-Manzanares, G. Guerrero-Trejo, J. C. Aguilar and J. Amador-Hernández, *ECS Trans.*, 3 (29) (2007) 73.
5. I. Bustero Y. Cheng, J. C. Mugica, T., Fernandez-Otero, F .A. Silva and D. J. Schiffrin, *Electrochim. Acta*, 44 (1998) 29.
6. A. V. Juarez, L.M. Yudi, *Electrochim. Acta*, 54 (2008) 530.
7. A. Benvidi, S. N. Lanjwani, Z. Ding, *Electrochim. Acta*, 55 (2010) 2196.
8. C. Baslak and T. Atalay, *Russ. J. Electrochem.*, 50(2) (2014) 200.
9. G. Lagger, L. Tomaszewski, M. D. Osborne, B. J. Seddon and H. H. Girault, *J. Electroanal. Chem.*, 451 (1998) 28.
10. A. Mastouri, S. Peulon, N. Bellakhal, A. Chaussé, *Electrochim. Acta*, 130 (2014) 818.
11. M. Alonso, A. Lopez-Delgado, A. M. Sastre, F. J. Alguacil, *Chem Eng J.*, 118 (2006) 213.
12. F. T. Minhas, S. Memon, I. Qureshi, M. Mujahid, M.I. Bhangar, *C. R. Chimie*, 16 (2013) 742.
13. J. A. Campbell, A. A. Stewart and H.H. Girault, *J. Chem. Soc., Faraday Trans. I*, 85(4) (1989) 843.
14. J. Zhang and P. R. Unwin, *Langmuir*, 18 (2002) 2313.
15. B.R. Silver, K. Holub, V. Mareček, *J. Electroanal. Chem.*, 784 (2017) 1.
16. M. L. Colombo, J. V. Sweedler, and M. Shen, *Anal. Chem.*, 87(10) (2015) 5095.
17. N. T. Iwai, M. Kramaric, D. Crabbe, Y. Wei, R. Chen and M. Shen, *Anal. Chem.*, 90(5) (2018) 3067.
18. M. Arooj, D. W. M. Arrigan, and R. L. Mancera, *J. Phys. Chem. B*, 123 (2019) 7436.
19. J. C. Aguilar, E. Rodríguez de San Miguel, J. de Gyves, R. A. Bartsch and M. Kim, *Talanta*, 54, (2001) 1195.
20. V. S. Markin and A. G. Volkov, *Electrochim. Acta*, 34(2) (1989) 93.
21. Y. Cheng, and D. J., Schiffrin, *J. Chem. Soc. Faraday Trans.*, 89(2) (1993) 199.
22. T. Osakai, T. Kakutani and M. Senda, *Bull. Chem. Soc. Japan*, 57 (1984) 370.
23. M. Velázquez-Manzanares and D. J., Schiffrin, *Electrochim. Acta*, 49 (2004) 4651.
24. B. R. Silver, K., Holub, V., Marecek, *J. Electroanal. Chem.*, 731 (2014) 107.
25. V. Marecek and Z., Samec, *Current Opinion in Electrochemistry*, 1 (2017) 133.
26. P. D. Beattie, A. Delay and H. H. Girault, *Electrochimica Acta*, 40(18) (1995) 2961.