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Electrochemical study of cations and anions transfer across water/1,2-dichloroethane interface facilitated by propylene carbonate

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ABSTRACT

In our work, the transfer reactions of four cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and seven anions (Br^-, NO_3^-, HPO_4^{2-} , SO_4^{2-}, CO_3^2, ClO_4^-, NO_2^-) across the micropipette supported water/1,2-dichloroethane (W/1,2-DCE) interface facilitated by propylene carbonate (PC) were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. Well-defined voltammetric behaviors were obtained for all ions. The electrochemical data were used to determine the thermodynamic parameters (diffusion coefficient, standard Gibbs energy of transfer, stoichiometric ratio and the apparent association constant) of the facilitated ion transfer processes.

Keywords: Solvation effect; Facilitated ion transfer (FIT); Aqeous complexation followed by transfer of the complex (ACT) mechanism; Propylene carbonate (PC); Micro and nano-liquid/liquid interface

1. Introduction

The widespread presence of ions in nature gives a big challenge to chemists worldwide. For instance, in nuclear waste streams and other groundwater contamination, the latter is often from detergents and agriculture-related processes, a variety of ions make their way into the environment [1–3]. Beside this, they play a basic role in many vital processes such as transport across cell membranes, homeostasis and processes associated with changes of energy [4,5]. Some of these ions are nitrates, phosphates, sulfates, carbonates, chloride, bromide, chlorate and metals ions. Therefore, more effective methods allowing rapid, selective, and inexpensive determination of ions in environment and industry are needed [4,6]. Many years ago, supramolecular chemistry was based mainly on the recognition and selective binding of cations [7,8]. In 1968, Park and Simmons synthesized the first anion receptor and few reports that use the liquid/liquid interface for studying hydrophilic anion transfer and their sensing applicability have been published [6,9–11]. However, this slow growth is probably due to the difficulties caused by the design of receptors capable of anion binding. Anions are larger than isoelectronic cations, which gives a lower charge to size ratio. This reduces the contribution of electrostatic interactions with the host [12,13]. Another challenge is the high solvation energy of anions, which means that the environment of complexation has a major impact on the process of molecular recognition [9]. Hydrophilic anions generally possess a very highly negative standard Gibbs energy of transfer that are similar to each other, which also usually limits the potential window at the negative potential, and it is thus difficult to distinguish each anion transfer reaction [14].

Dietrich et al. [15] postulated that compounds capable of binding ions can be divided into several groups depending

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on the type of ion interactions. Ligands (ionophores) may be presented in neutral form or charged form. Charged ligands bind substrate via electrostatic interactions, whereas neutral ligands form complex mainly through oxygen [16], sulfur [17], nitrogen [18] and hydrogen interaction [19].

Facilitated ion transfer (FIT) reactions are very important class of reactions which involve the transfer of ion and ligand between two immiscible liquid phase. Koryta became the father of FIT reaction since 1979 [20]; he reported the facilitated transfer of potassium and sodium ions from the aqueous phase by the dibenzo-18-crown-6 polyether into the oil phase. Based on such publication, several researchers stipulated the thermodynamic and kinetic information, and explained the applications of FITs in modern analytical chemistry, medicine, technology, environmental protection, selective amperometric ion sensors and in electro-assisted solvent extraction across liquid membranes [21–23].

The process of FIT occurs when an ion has relatively higher Gibbs energy of transfer at a liquid/liquid interface, and the ligand (ionophore) can be distributed on either side of the interface to decrease the Gibbs energy [24]. The transfer wave of ion normally appears outside of the potential window. Thus, its transfer can be adjusted to be within the potential window. Various ionophores, such as crown ethers, antibiotics, and calixarenes, have been examined to assist ions transfer [1,18,25]. The physico-chemical properties of the ion-ligand complex (association constant, charge, diffusion coefficient, and stoichiometry of the formed complex) determine the nature of the mechanism of charge transfer process across the liquid/liquid interface [26]. It consequently follows that the complexation reaction may be located either in the aqueous phase or in the organic phase, and that the complex can be formed either before or after the transfer [27].

In 1993, Girault and his team [28] postulated four possible mechanisms for FIT reactions by referring on the distribution coefficient of the ligand.

- Aqueous complexation followed by transfer of the complex (ACT)
- Transfer by interfacial complexation (TIC)
- Transfer by interfacial dissociation (TID)
- Transfer followed by organic phase complexation (TOC)

Among these four mechanisms, ACT is more interesting due to its special behavior whereby the ligand should be soluble in both phases and the ion-ligand complex is formed in aqueous phase.

Alkalines and alkalines-earth metals associated with macrocycles are also widely studied due to their application in analytical determination of these metals using potentiometric or amperometric (ion selective electrodes). As a consequence of the great variety of metals, ligands and experimental conditions used, diverse results have been obtained indicating that the transfer mechanisms can be of a different nature [26].

The first example of facilitated anion transfer (FAT) has been studied by Shioya [29] which is a hydrogen-binding ionophore for facilitated sulfate transfer by polarography. Later on, several researchers started to study anions transfer across two immiscible liquid phases [1,10,30–32].

Basically, complexation reactions at liquid/liquid interfaces contribute much more in the study of biochemical systems such as transmembrane signaling and enzymatic reactions in biological membranes. They are also applied in many technological systems like solvent extraction, phase transfer catalysis, chemical sensors, energy storage and conversion and other fields [18,33].

In the study conducted by Nestor et al. [18,34], it was reported that PC can play a role of ligand to facilitate Li^+ ion transfer across W/1,2-DCE interface and has been shown that this process follows ACT mechanism. However, no study has been reported regarding anions transfer facilitated by PC.

As electrochemical study on interface between two immiscible electrolytes solution (ITIES) developed, and most researches deal with the FIT across water/oil interface. The synthetic (crown ethers) and natural (valinomycin) ligands have been used as ionophore to assist the transfer of ions. The high cost, high toxicity and the sophistication of synthesis are main characteristic of these ligands, which limit their application in solvent extraction, phase transfer catalysis, chemical sensors, and energy storage and conversion [9,35].

To solve such problems, PC with the chemical formula $C_4H_6O_3$ which is slightly soluble in water and strongly soluble in polar organic solvents can be used and play the same function as the existing ligands. In this research, we note that PC is used to facilitate the transfer of cations and anions between two immiscible phases and plays the role of selective agent to detect ions which are in the same system using cyclic and differential pulse voltammetry (DPV) techniques.

2. Materials and methods

All of the electrochemical measurements described in this work were performed at ambient temperature (23°C ± 2°C) in a Faraday cage. CV and DPV at the liquid/liquid interface were recorded with a CHI 760D electrochemical work station (CH Instruments Inc., USA).

An Ag/AgCl wire was inserted into the aqueous phase inside the micropipette as the aqueous reference electrode. An Ag/AgTPBCl wire was immersed in the outside organic phase as the organic reference electrode (refer to the supporting information, Fig. 1). The obtained electrochemical data were analyzed with Origin Pro v8 software (Origin Lab Co., Northampton, USA).

To obtain the electrochemical measurement, the used electrochemical cell for the transfer of ions facilitated by PC solvent can be represented as follows:

Cell 1

$$\begin{aligned}&\mathrm{Ag}\left|\mathrm{AgTPBCl}\right|5\ \mathrm{m\ mol/L\ BTPPATPBCl}+1{,}2\quad \mathrm{DCE}+\\&\mathrm{PC}\parallel 2\ \mathrm{m\ mol/L\ TMACl}+\mathrm{y\ m\ mol/L\ MCl}\mid C_{\mathrm{PC}}\\&=6\ \mathrm{m\ mol/L},\mathrm{y}=1\ \mathrm{m\ mol/L}\end{aligned}$$

Cell 2

$$\begin{aligned}&\mathrm{Ag}\left|\mathrm{AgTPBCl}\right|5\ \mathrm{m\ mol/L\ BTPPATPBCl}+1{,}2\quad \mathrm{DCE}\\&+\mathrm{PC}\parallel 2\ \mathrm{m\ mol/L\ TMACl}+\mathrm{m\ mol/L\ NaZ}\mid \mathrm{Ag}\mid C_{\mathrm{PC}}\\&=6\ \mathrm{m\ mol/L},\mathrm{y}=5\ \mathrm{m\ mol/L}\end{aligned}$$

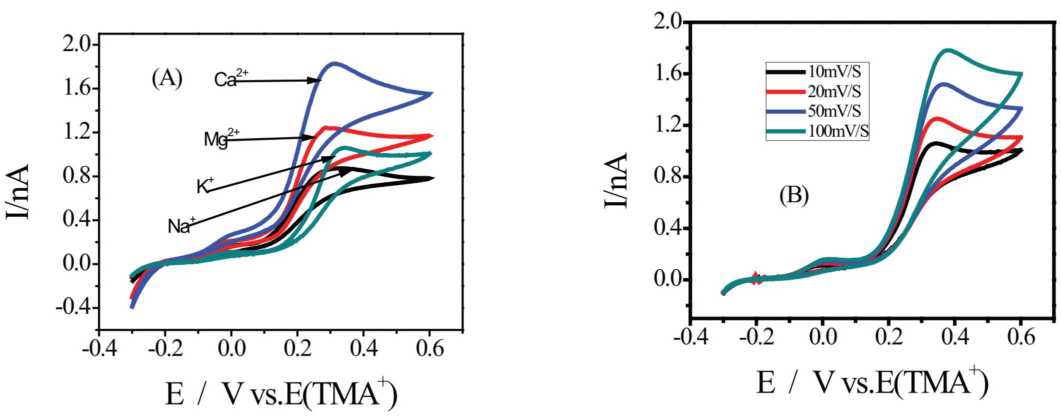

Fig. 1. The cyclic voltammetry of ions transfer across water/1,2-DCE interface facilitated by PC with Cells 1. (A) Cations transfer, the concentration of M is 1 mmol/L; (B) CV of Mg^{2+} ion transfer at different scan rate.
Note: The volume ratio of 1,2-DCE over PC is 3:1, scan rate is 50 mV/s, and the diameter of micropipette is 8 μm.

Cell 3

$$\mathrm{Ag}\left|\mathrm{AgTPBCl}\right|5\ \mathrm{m\ mol/L\ BTPPATPBCl} + 1,2\text{-}\mathrm{DCE} + \mathrm{PC} \,\|\, 2\ \mathrm{m\ mol/L\ TMACl}y\ \mathrm{m\ mol/L\ NaClO_4} \mid C_{PC} = 6\ \mathrm{m\ mol/L}, y = 2\ \mathrm{m\ mol/L}$$

Cell 4

Ag | AgTPBCl | 5 m mol/L BTPPATPBCl + 1, 2-DCE + PC ($V_{1,2\text{-DCE}}$: V_{PC} = X) ‖ 2 m mol/L TMACl + 0.3 m mol/L MZ | Ag Cpc = 0.3, 0.9, 1.8, 3.6, 6 m mol/L Z and M represent (CO_3^{2-}, Br^-, NO_2^-, NO_3^-, SO_4^{2-}, HPO_4^{2-} and Na^+)

where ‖ represents the W/1,2-DCE interface, C_{PC} is the concentration of PC in organic phase which is corresponding to PC:1,2-DCE volume ratio 1/99, 1/19, 1/9, 1/4, 1/3 in discussion part, *y* is the concentration of ions in water phase. BTPPATPBCl represents bis-(triphenylphosphoranylidene) ammonium chloride, and TPBCl represents trerakis-(4-chlorophenylborate).

3. Results and discussion

3.1. Study cyclic voltammetry (CV)

Firstly, CV was employed to characterize the transfer process of ions (Br–, NO_3^-, HPO_4^{2-}, SO_4^{2-}, CO_3^{2}, ClO_4^-, NO_2^- anions and Na^+, K^+, Mg^{2+}, Ca^{2+} cations) across the polarized micro-W/1,2-DCE interface with an aqueous internal reference cation, tetramethylammonium (TMA^+) ion.

From Fig. 1(A) and (B) and Fig. 2, waves connected with the transfer of ions from the aqueous phase to the DCE phase were observed in the presence of PC. The CV obtained using Cell 1 with *M* equal to metal ion is shown in Fig. 1(A) with an initial potential of –0.3 V, from which the potential was swept at a rate of 0.050 V/s in the forward direction towards more positive potentials until 0.6 V was reached. During this initial segment, the peak shaped waves were observed at 0.3 V and were attributed to M-PC complex transfer from water to DCE. From Fig. 1(B), we observed that the scan rate varies with peak current.

It can be observed that the anodic segment was a peak shape but the cathodic segment was sigmoidal. Actually, at the micropipette supported interface, the diffusion field is linear for ion transfer egress the micropipette but hemispheric for ion transfer ingress the micropipette. Although PC is an organic solvent and totally miscible with 1,2-DCE, it has a little solubility in water with a molar ratio of 3.6% [36]. Ion complex with the PC molecules dissolved in aqueous phase and then transfers into the 1,2-DCE phase. This process is exactly the ACT mechanism, i.e., aqueous complexation followed by interfacial transfer, suggested by Shao and Girault [37].

There is also another small peak appeared at 0.00 V which corresponds with the TMA^+ ion introduces into the aqueous solution and the variation of scan rate has no influence on the current generated by TMA^+.

Contrary to TIC, TID and TOC mechanisms, the ACT mechanism is the easiest when studying the transfer of ion across two immiscible phase, because the voltammetry resulting from such mechanism have the peak shape as the one obtained for the macro-ITIES [38]. The CV obtained using cell 2 is illustrated in Fig. 2, where Z corresponds to anion. In order to do so, a more negative potential was applied to the system and a peak shape wave was observed at 0.6 V during forward direction which indicates the transfer of Na-PC complex from Water to DCE. Another peak wave was observed in the reverse direction at more negative potential which indicates the transfer of Z-PC complex from Water to DCE. The high negative current obtained reflects to the transfer of anions from one phase to another. The small peak obtained about 0.2 V represents the TMA^+ ion introduced into the aqueous phase, these peak is confirmed by the low positive current observed at 0.2 V.

This mechanism of anion transfer is confirmed based on information got from other literatures. As example, in 2012, Stockmann at al. [39] investigated the transfer of both Cesium(Cs^+) and Nitrate (NO_3^- ions using CV. In their study, two peaks were observed correspond to Cs^+ and NO_3^- ions.

Some information regarding ion transfer, like diffusion coefficient, stoichiometric ratio, association constant, half-wave potential and the Gibbs transfer energy are evaluated based on their voltammetric responses. One of the conventional methods to determine the thermodynamic properties of ion transfer occurring across a polarized liquid/liquid

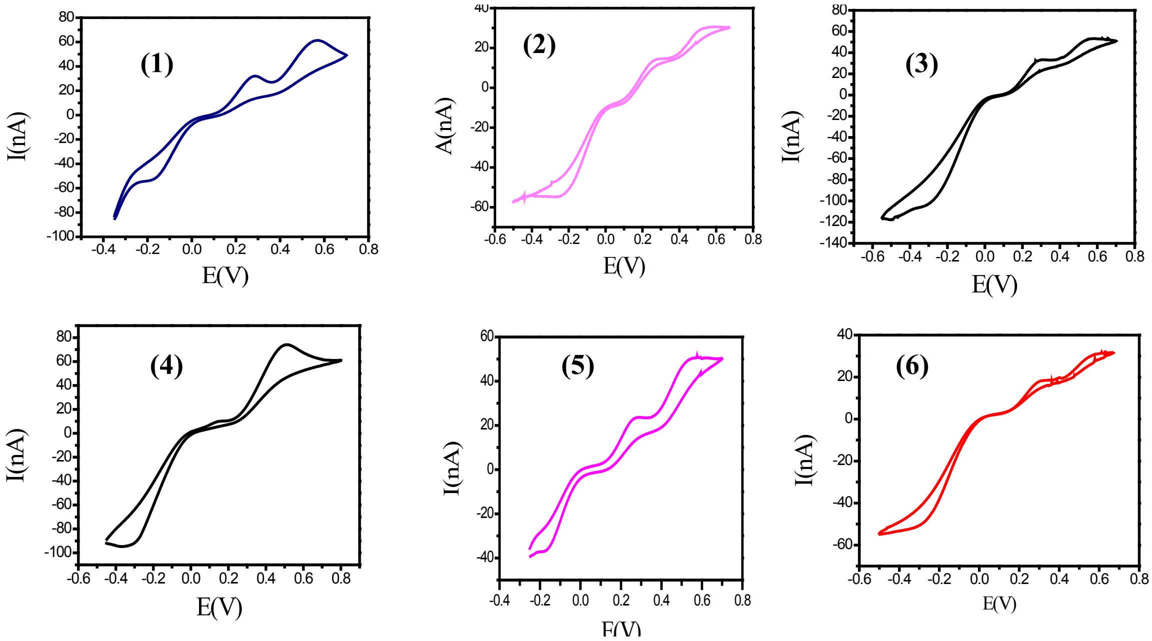

Fig. 2. The cyclic voltammetry of anions transfer across water/1,2-DCE interface facilitated by PC with Cells 2, the concentration of Z is 5 mmol/L; the numbers 1, 2, 3, 4, 5, 6 indicate the CV of sulfate, perclorate, hydrogenphosphate, nitrate, carbonate and bromide anions respectively.
The volume ratio of 1,2-DCE over PC is 3:1, scan rate is 50 mV/s, and the diameter of micropipette is 8.

interface is the use of standard thermodynamic values of well characterized reference ions [40] such as TMA^+. Therefore, the TMA^+ ion was used as an internal reference in order to estimate the half-wave potential and the Gibbs transfer energy values of hydrophilic ions in accordance with the TATB estimation using the following expression [9].

$$\Delta_O^W\varnothing_{1/2,I} = \Delta_O^W\varnothing_{1/2,I(\mathrm{exp})} - (\Delta_O^W\varnothing_{1/2,TMA^+(\mathrm{exp})} - \Delta_O^W\varnothing^{0'}_{TMA^+}) \quad (1)$$

where $\Delta_O^W\varnothing^{0'}_{TMA^+}$ is the formal potential and it is equal to 160 mV at the W/1,2-DCE interface [41], $\Delta_O^W\varnothing_{1/2,TMA^+(\mathrm{exp})}$ is the half wave potential of TMA^+, $\Delta_O^W\varnothing_{1/2,I}$ is the half wave potential of ions transfer from water to the organic phase.

The energy needed to transfer ions from one phase to another is dependent on the difference between dehydration and resolvation energies and is related to the difference of electrochemical potential applied to two adjacent phases when the ion transfer occurs. The difference between the Gibbs energies of hydration and solvation is effectively the work that is required transferring an ionic species, *I*, from the bulk aqueous phase (*w*) to the bulk organic phase (*o*). This Gibbs energy of transfer $\Delta_O^W G_{tr,I}^{W\to O}$ for the specified ion of interest is related to the energy potential of transfer $\phi_{0.}$

$$\Delta_O^W G_{tr,I}^{W\to O} = Z_I F \Delta_O^W\varnothing_{1/2,I} \quad (2)$$

where *Z* and *F* are the number of ions transferred and the Faraday constant, $\Delta_O^W G_{tr,I}^{W\to O}$ is Gibbs transfer energy commonly used are related to ion transfer between mutually saturated solvents (known as the Gibbs energy of partition).

Table 1
Thermodynamic data of cation transfer facilitated by PC

Cation	$\Delta_O^W\varnothing_{1/2,1}$ (V)	$\Delta_O^W G_{tr,1}^{W\to O}$ (Kj/mol)	$D_{1\text{–}PC}$ cm²/s
Na^+	0.42	40.5	1.88×10^{-5}
K^+	0.44	42.45	1.76×10^{-5}
Ca^{2+}	0.472	91	1.42×10^{-5}
Mg^{2+}	0.46	88.7	1.69×10^{-5}
Average			1.68×10^{-5}

We noted that Na^+ and Mg^{2+} ions show the lower free energy of transfer in each group, and a stronger interaction with PC is expected for these cations. That is the relationship between transfer potential and the association constant. From Fig. 2(B), it was observed that the peak current increased up 1.8 nA for Mg^{2+} transfer when the scan rate changed from 10 mV/s to 100 mV/s. The similar electrochemical behaviors were observed for the other three ions as observed from Fig. 7 of supplementary information (SI).

The relationship between peak current and scan rate resulted the way to calculate the diffusion coefficient (refer to Eq. (1) SI) for all cations as indicated in Table 1. The values obtained are in the same order of magnitude with the values reported in ref. [18,34].

The more negative value of the Gibbs transfer energies for FAT indicates that a more negative applied potential is required so that the anions move from the aqueous to the organic phase or vice versa take place.

Based on Fig. 2, results showing that the negative values of the Gibbs transfer energies increase in this order: $CO_3^{2-}, Br^-, NO_2^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}$ (Table 2) and they are in accordance with the lipophilicity sequences of anions in the Hofmeister series [42].

3.2. Investigation of the possibility of fabrication of ion sensors

Fig. 3 illustrates the transfer of both Na^+ and ClO_4^- ions from water to 1,2-dichloroethane interface facilitated by propylene carbonate (PC). We observed the variation of peak current for both ions (Na^+ and ClO_4^-) as the scan rate increased. ACT mechanism was deduced based on the shape of voltammetry as $C_{PC} >> C_I$. This enabled us to determine the diffusion coefficient of anions as indicated in Table 2 and the values of diffusion coefficient obtained are in the same validation with the ones reported by Shao and his team [9]. It is important to note that the same process has been obtained for all other six anions by referring to the SI Fig. 8.

3.2.1. Cation

The main criterion which must be taken into account to make amperometric sensor is that the concentration of ligand in organic phase should be in excess to that of ions in the aqueous phase. To our case, the concentration of PC was greater than the concentration of Na^+. The typical CV depicted in Fig. 4 was obtained. The volume of PC: DCE was in 1:3, 1:6, 1:9, 1:15 ratio and concentration of Na^+ was 0.8 mM at the sweep rate of 0.050 V/s.

Table 2
Thermodynamic data of anion transfer facilitated by PC

Anion	$\Delta_O^W \varnothing_{1/2,1}$ (mV)	$\Delta_O^W G_{tr,1}^{W\to O}$ (Kj/mol)	$D_{I\text{-}PC}$ cm²/s
Br^-	–261.6	–25.23	3.2×10^{-6}
ClO_4^-	–130.4	–12.41	1.09×10^{-6}
NO_3^-	–274	–28.7	1.19×10^{-6}
HPO_4^{2-}	–325	–60.85	3.9×10^{-6}
SO_4^{2-}	–292	–36.2	1.57×10^{-6}
CO_3^{2-}	–298.7	–37.3	2.3×10^{-6}
Average			2.2×10^{-6}

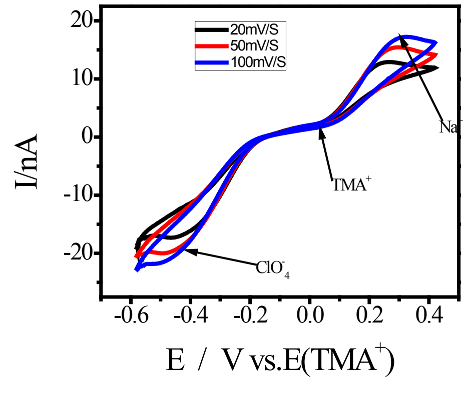

Fig. 3. The cyclic voltammetry of Na^+ and ClO_4^- ions transfer across water/1,2-DCE interface facilitated by PC with Cell 3.

The diffusion coefficient of Na^+ ion in the aqueous phase was calculated to be equal 1.8×10^{-5}cm²/s, which is in good validation with the value reported in ref [18].

Using the half wave potential and log (C_{PC}) relationship, the stoichiometric ratio has been evaluated and was equal to 1:3. Consequently, $Na(PC)_3^+$ complex is formed in aqueous phase.

It is very difficult to study separation of cations based on half-wave potential using CV. Therefore, a more efficient technique to select ions even at low concentration is recommended. The DPV is used to select two or more ions which are presenting in the same environment. From Fig. 5, the selection of Na^+ ion from its mixture with Mg^{2+} and K^+ has been illustrated.

The detection of Na^+ ion in the excess of Mg^{2+} and K^+ ions is a challenging task using CV technique. An alternative technique DPV is used to increase the selectivity of Na^+ ion transfer over that of its cousins Mg^{2+} and K^+ ions. From Fig. 5, the potential (0.56 mV, 0.76 mV and 1.16 mV) correspond to Na^+, K^+, Mg^{2+} ions were evaluated respectively. Here the TMA^+

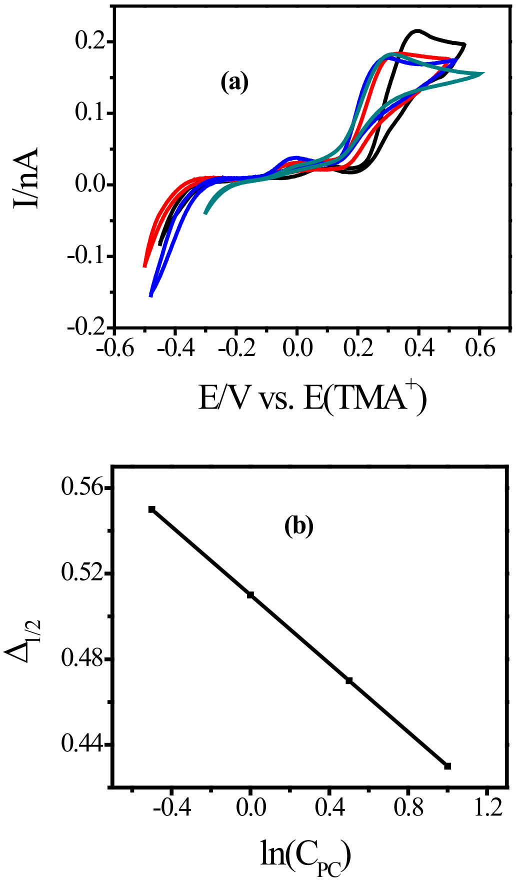

Fig. 4. (a) The voltammetry of PC facilitated Na^+ ion transfer across the water/1,2-DCE interface with $V_{PC}/V_{1,2\text{-}DCE}$ ratio of 1/3 (black curve), 1/6 (red curve), 1/9 (blue curve), and 1/15 (green curve) at scanning rate of 0.05 V/s. (b) Logarithmic relationship between the half-wave potential and the molar concentration of PC in 1,2-DCE phase.

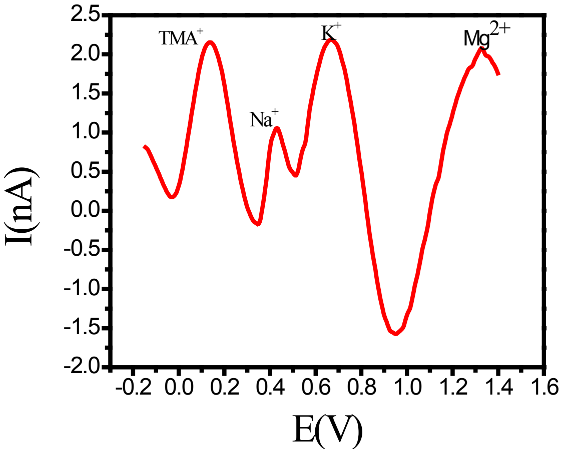

Fig. 5. DPV of PC facilitated Na^+ (1 mM), K^+ (3 mM) and Mg^{2+} (3 mM). Amplitude, pulse width, sample width, pulse period and quit time are 0.05, 0.05, 0.0167, 0.2 and 2, respectively.

was also used as the internal reference cation for calibration and the peak corresponds with this ion is about 0.1 V. It can be seen that the selective sensitivity of PC for Na^+ ion took place first compared with that of K^+ and Mg^{2+} even if the concentrations of Mg^{2+} and K^+ were over 3 orders of magnitude in excess. It is the indication of how PC can be used to make sodium ion sensor which does not interfere with Mg^{2+} and K^+ ions. It was also highlighted that a more negative peak observed between Mg^{2+} and K^+ ions illustrated a great separation between these two ions even if they present the same concentration in the studied environment.

3.2.2. Anions

We were also interested in verifying the behavior of CV when the concentration of anions was kept constant (0.3 mM), the volume ratio of PC:DCE were varied in the range of 1/3, 1/4, 1/9, 1/19, 1/99 relate to 25%, 20%, 10%, 5% and 1% percentages of PC in DCE. Fig. 6(a) shows the obtained CV at different PC:DCE volume ratio.

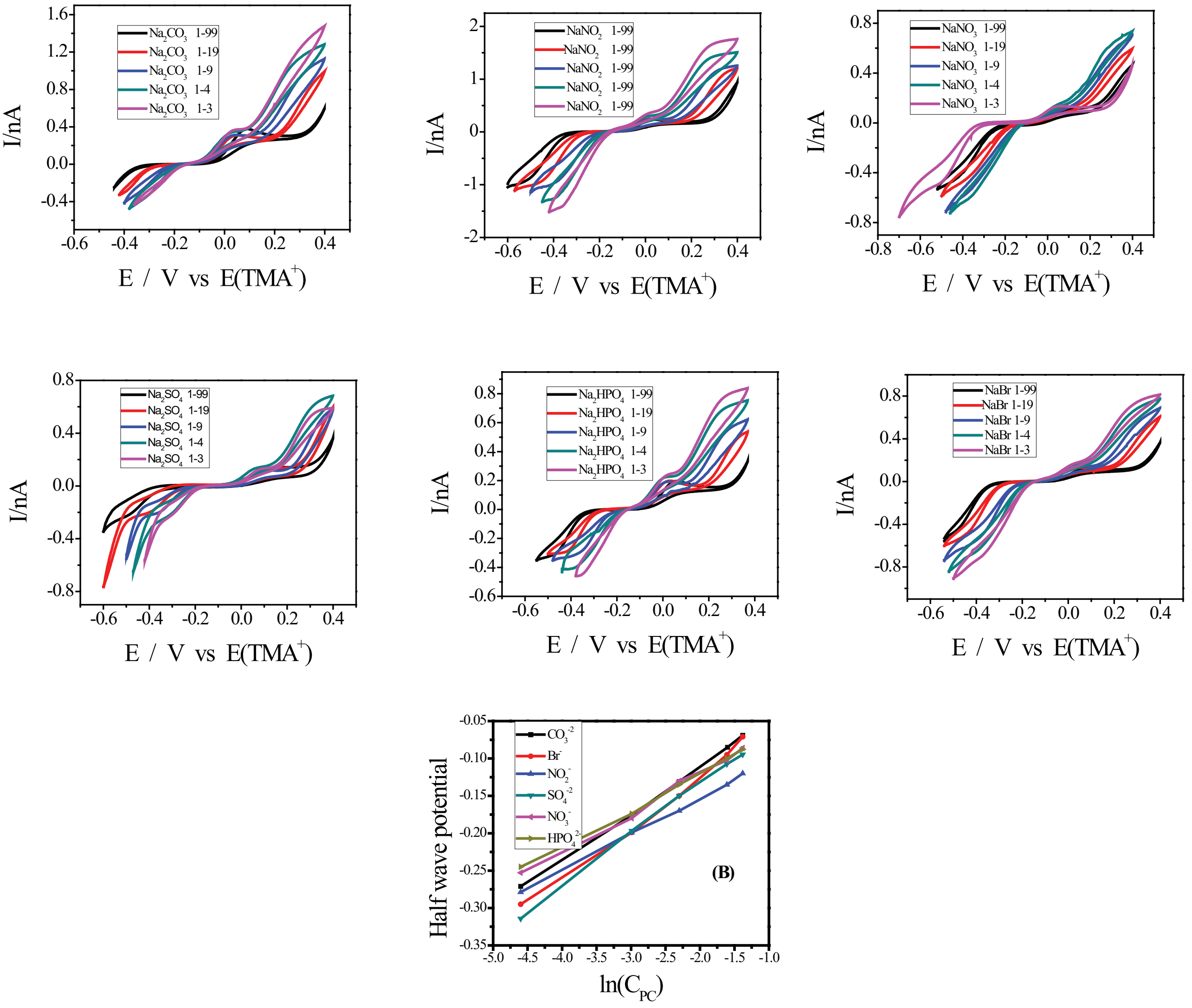

Fig. 6. The CV of PC facilitated anion transfer across water/1,2-DCE interface with $V_{PC}/V_{1,2\text{-}DCE}$ ratio of 1/3, 1/4, 1/9, 1/19 and 1/99 at scanning rate of 0.05 V/s (b) Logarithmic relationship between the half-wave potential and the molar concentration of PC in 1,2-DCE phase.

As confirmed in refs. [24,34], the transfer potentials shift to lower values, when increasing the concentration of ionophore and maintaining the concentration of ion constant. In our study, it was observed that as the concentration of ion was constant and varies the PC:DCE volume ratio, the transfer potentials values shifted to a low negative value and the best choice PC:DCE volume ratio for the next experiment (Fig. 7) was examined to be 1/99 which resulted the best peak wave voltammetry.

Fig. 6(a) illustrates clearly the FATs within the potential window when PC was used as a ligand (ionophore). This caused by the association constants between PC and anions are big enough to facilitate anion transfers to an observable potential within the potential window.

As noted in the publications by Shao et al. [9] and Sun et al. [43], a 1:1 complex between ligand and various anions is formed in organic phase under the ACT mechanism. In their studies, the concentration of anions was greater than the concentration of ligand. A linear relationship between the concentration of an anion and the half wave potential of the FAT was announced.

In our work, the concentration of anions was lower than the concentration of PC in DCE, and the different volume ration of DCE over PC (1/3, 1/4, 1/9, 1/19, 1/99) have been used to detect the transfer of anions. It is important to note that the anion-PC complex is formed in aqueous phase and this allow the use of Eq. (2) found in supporting information to calculate the stoichiometric ratio and association constants.

The Plot of E versus log C_{PC} gave rise to six linear relationships for the respective six anions (see Fig. 6(b)). From the slopes 0.06262, 0.06878, 0.04854, 0.052, 0.06845, 0.04908 values were deduced for CO_3^{2-}, Br^-, NO_2^-, NO_3^-, SO_4^{2-}, HPO_4^{2-} anions respectively and are close to the values reported in ref. [9]. It was concluded that the 1:1 and 1:2 stoichiometric ratio between the anion and PC are formed for NO_3^-, Br^-, NO_2^-, NO_3^- and CO_3^{2-}, SO_4^{2-}, HPO_4^{2-}, respectively. This finding has also been investigated through the work carried out in ref. [44] for mono anion and no report shows the 1:2 ratio between anion and PC has been published. This ratio is assumed to be true based on the charge of anions tested (CO_3^{2-}, SO_4^{2-}, HPO_4^{2-}).

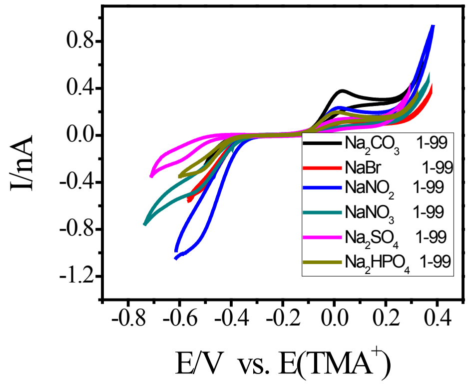

Fig. 7. The CV of PC facilitated anion transfer across water/1,2-DCE interface with $V_{PC}/V_{1,2\text{-}DCE}$ ratio is 1/99 at scanning rate of 0.05 V/s.

From the intercepts, the association constants corresponding to the interaction between the anions and PC were calculated as 4.78, 5.77, 5.22, 4.69, 5.42, 4.3 for CO_3^{2-}, Br^-, NO_2^-, NO_3^-, SO_4^{2-}, HPO_4^{2-} respectively. These values are in good validation with the ones presented in previous reports [9,18].

DPV technique is not only limited for cations, it can also be used to study selective sensitivity of anions. Fig. 8 shows DPV of the selective transfer of ClO_4^- over NO_3^-. Here the TMA+ was also used as the inner reference aqueous cation. The more negative potential deals with the nitrate anion and by observing their half wave potential, it can be concluded that the selective sensitivity of PC for ClO_4^- ion is higher than that of trigonal nitrate ion.

The last point was to investigate the selectivity of NO_2^- in its mixture with Cl^- ion. 25% of PC in DCE was used. As a result, there was a real separation potential of these two ions. One appeared at –0.1 mV which was attributed to Cl^- ion, while another occurred at –0.225 mV corresponded to NO_2^- ion. Based on Fig. 9, a clear separation between peak currents of these two anions was marked; we observed that Cl^- ion was not interfere with NO_2^- ion when they were in the same system. An additional peak observed at more negative potential around –0.5 V was attributed to the simple transfer of nitrite ion.

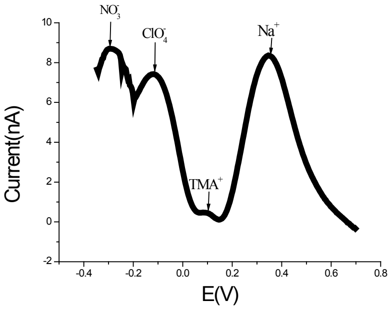

Fig. 8. DPV of ClO_4^- and NO_3^- across W/1, 2-DCE interface facilitated by PC. ClO_4^- (1.5 mM) and NO_3^- (3 mM). Amplitude, pulse width, sample width, pulse period and quit time are 0.05, 0.05, 0.0167, 0.2 and 2, respectively.

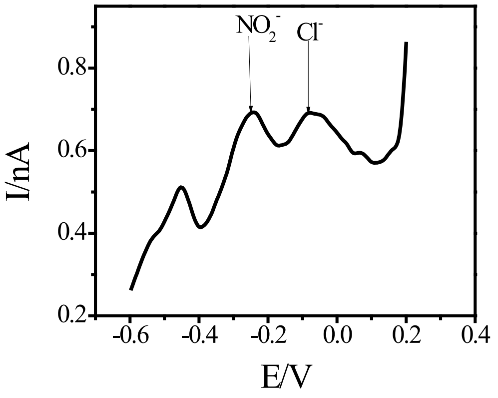

Fig. 9. The selectivity of NO_2^- in its mixture with Cl^- ion by PC. The concentration of NO_2^- (1 mM) and Cl^- (1 mM), the DCE:PC ratio is 1/3 and amplitude, pulse width, sample width, pulse period and quit time are 0.05, 0.05, 0.0167, 0.2 and 2, respectively.

4. Conclusion

In summary, we have demonstrated the FIT of seven anions, namely Br^-, NO_3^-, HPO_4^{2-}, SO_4^{2-}, CO_3^2, ClO_4^-, NO_2^- and four cations Na^+, K^+, Mg^{2+}, Ca^{2+}, by PC at a micro-W/1,2-DCE interface. We have also investigated for the first time that the dynamics of this process can be studied by micropipette voltammetry. Such studies are expected to be useful in understanding the mechanism of ion transport at a polarized interface and for the design of yet-improved ion receptors and carriers. The application of DPV to the ITIES experiment was shown to be superior to the CV in detecting ion transfer. The application of ITIES to ion analysis and DPV to ITIES analysis is thus extended.

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Supporting Information

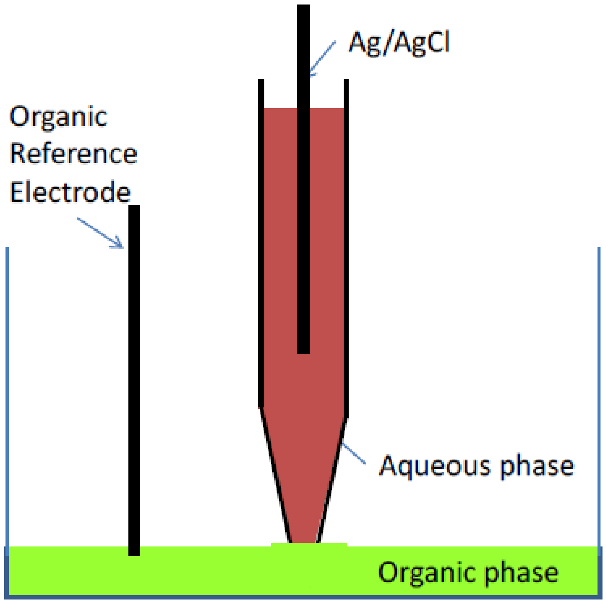

Fig. 1. Schematic representation of voltammetric experiment at a nano-microscopic L/L interface supported at a tip of nano-micropipette.

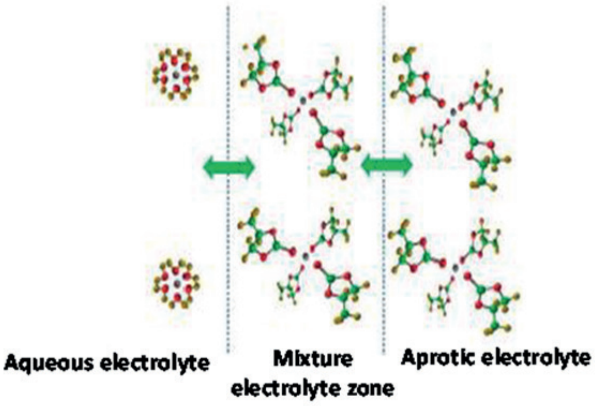

Fig. 2. Schematic diagram of facilitated ion transfer across water/1,2-DCE+PC interface.

The high dielectric constant, high polarity, low toxicity and the ability to form complex with Lithium ion make many researchers to use propylene carbonate (PC) as the promising candidate. Due to its high relatively boiling point, it is combined with other polar organic solvents and water to form safe solvent system. The PC with the chemical formula $C_4H_6O_3$ is slightly soluble in water and strongly soluble in polar organic solvents.

$$i_p = 0.4463 \times 10^{-3} n^{3/2} F^{3/2} A \left(RT\right)^{-1/2} D^{1/2}_{\mathrm{I(PC)}_z^+} C v^{1/2} \tag{1}$$

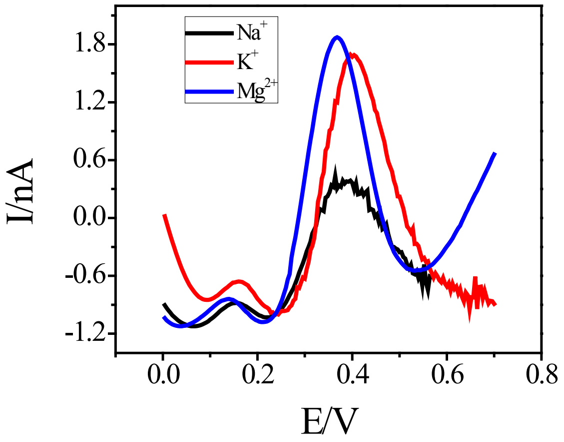

Fig. 3. The DPV of ions transfer across water/1,2-DCE interface facilitated by PC with Cells 1. The concentration of M is 1 mmol/L.

where i_p is the peak current, n is the number of transferred charge, F is the Faraday constant, $D_{I(PC)z+}$ is the apparent diffusion coefficient of $\mathrm{I(PC)}_z^+$ ion, a is the radius of micropipette orifice, C is the apparent concentration of $\mathrm{I(PC)}_z^+$ ion.

$$\Delta_{\mathrm{O}}^{\mathrm{W}} \varphi_{\mathrm{I\text{-}PC}}^{1/2} = \Delta_{\mathrm{O}}^{\mathrm{W}} \varphi_{I}^{1/2} + \frac{RT}{F} \ln\left(\frac{\beta_{\mathrm{m}}^{\mathrm{w}}}{\beta_{\mathrm{m}}^{\mathrm{o}} \left(P_{\mathrm{PC}}\right)^{Z}} \right) \tag{2}$$

where $P_{\mathrm{PC}} = C_{\mathrm{PC}}^{\mathrm{O}} / C_{\mathrm{PC}}^{\mathrm{W}}$, $\Delta_{\mathrm{O}}^{\mathrm{W}} \varphi_{\mathrm{I\text{-}PC}}^{1/2}$ and $\Delta_{\mathrm{O}}^{\mathrm{W}} \varphi_{\mathrm{I}}^{1/2}$ are the half-wave potential of $I(\mathrm{PC})_z^+$ and ion transfer across water/1,2-DCE interface, $\beta_{\mathrm{m}}^{\mathrm{w}}$ and $\beta_{\mathrm{m}}^{\mathrm{o}}$ are association constant of $I(\mathrm{PC})_z^+$ ion in each bulk phase, z is the stoichiometric number of $I(\mathrm{PC})_z^+$ ion.

We can get the message from Fig. 5 of how the concentration of both nitrite and sodium ions varies with the current. Different concentration of sodium and nitrite ions have been used to check the change of current with concentration (0.01 Mm, 0.1 mM, 0.5 mM, 1 mM). We already know that the peak current increases as the concentration of limiting species increases, when CV technique is used.

The same story has been observed for the case of DPV method and this is more advantageous because it can be used even for very small quantity of species of interest. As the concentration of both ions increases (Na^+, NO_2^-), the characteristic peaks current also increased and the maximum value of current was almost equal to 1.8 nA for Na^+ and 1.25 nA for NO_2^- which correspond to 1 mM.

As can be seen from Fig. 6, besides the facilitated transfer potential of Na^+ obtained at 400 mV, the facilitated transfer potential of Ca^{2+} ion was observed at 530 mV under the same experimental conditions simultaneously.

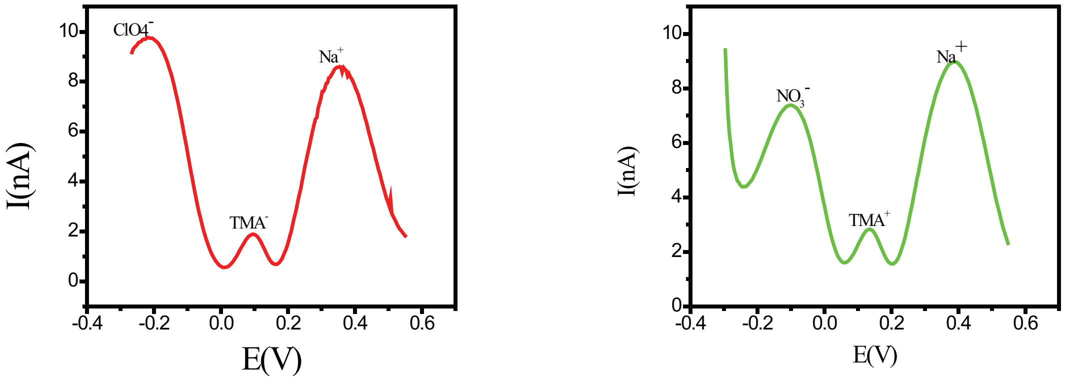

Fig. 4. DPV of ClO_4^- and NO_3^- across W/1, 2-DCE interface facilitated by PC. ClO_4^- (3 mM) and NO_3^- (3 mM). Amplitude, pulse width, sample width, pulse period and quit time are 0.05, 0.05, 0.0167, 0.2 and 2, respectively.

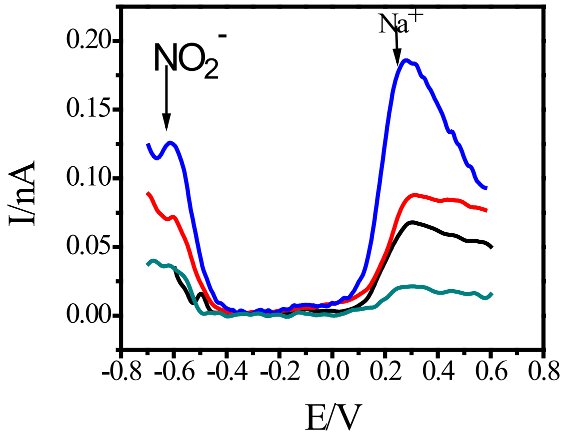

Fig. 5. The dependence of Current on $NaNO_2$ concentration using DPV technique. The concentration of $NaNO_2$ (0.01 mM, 0.05 mM, 0.1 mM, 0.5 mM), the DCE:PC ratio is 1/99 and amplitude, pulse width, sample width, pulse period and quit time are 0.05, 0.05, 0.0167, 0.2 and 2, respectively.

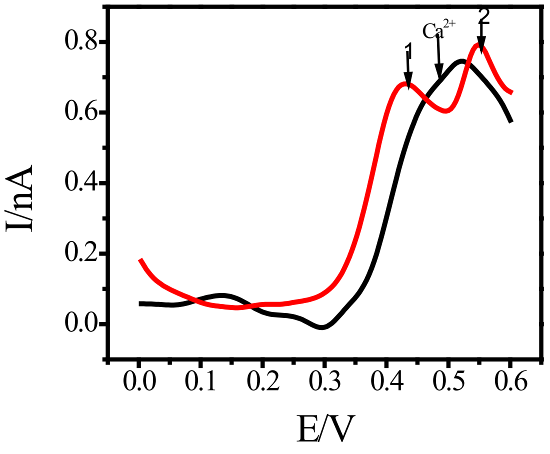

Fig. 6. Differential pulse voltammograms of the facilitated transfer of Na^+ in the presence of Ca^{2+} when the volume ratio of DCE:PC is 1/9 and the concentration of both cations is 0.8 Mm.

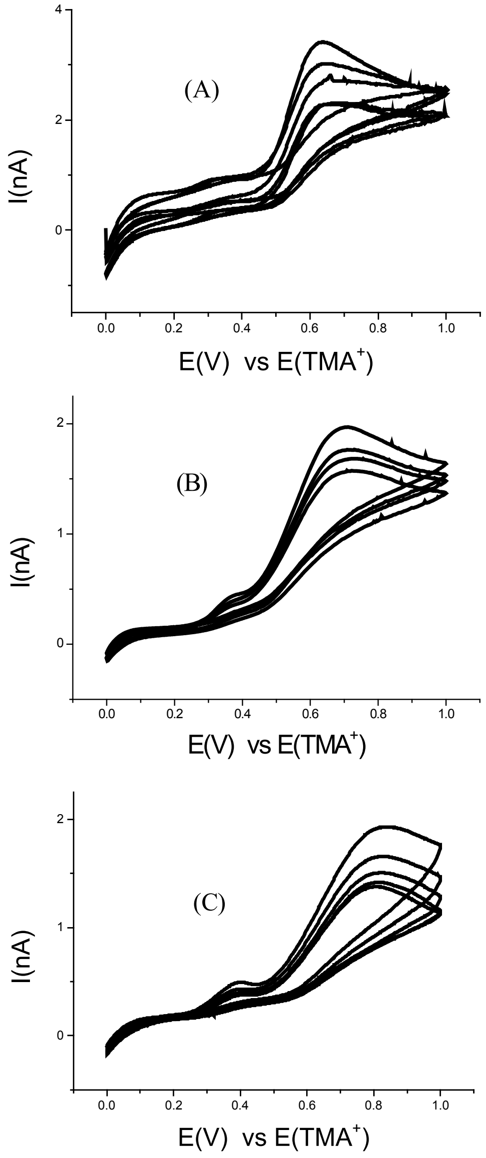

Fig. 7. CV of K^+ (C), Na^+ (B), Ca^{2+} (A) ion transfer at different scan rate. The volume ratio of 1,2-DCE over PC is 3:1, scan rate is 50 mV/s, and the diameter of micropipette is 8 µm.

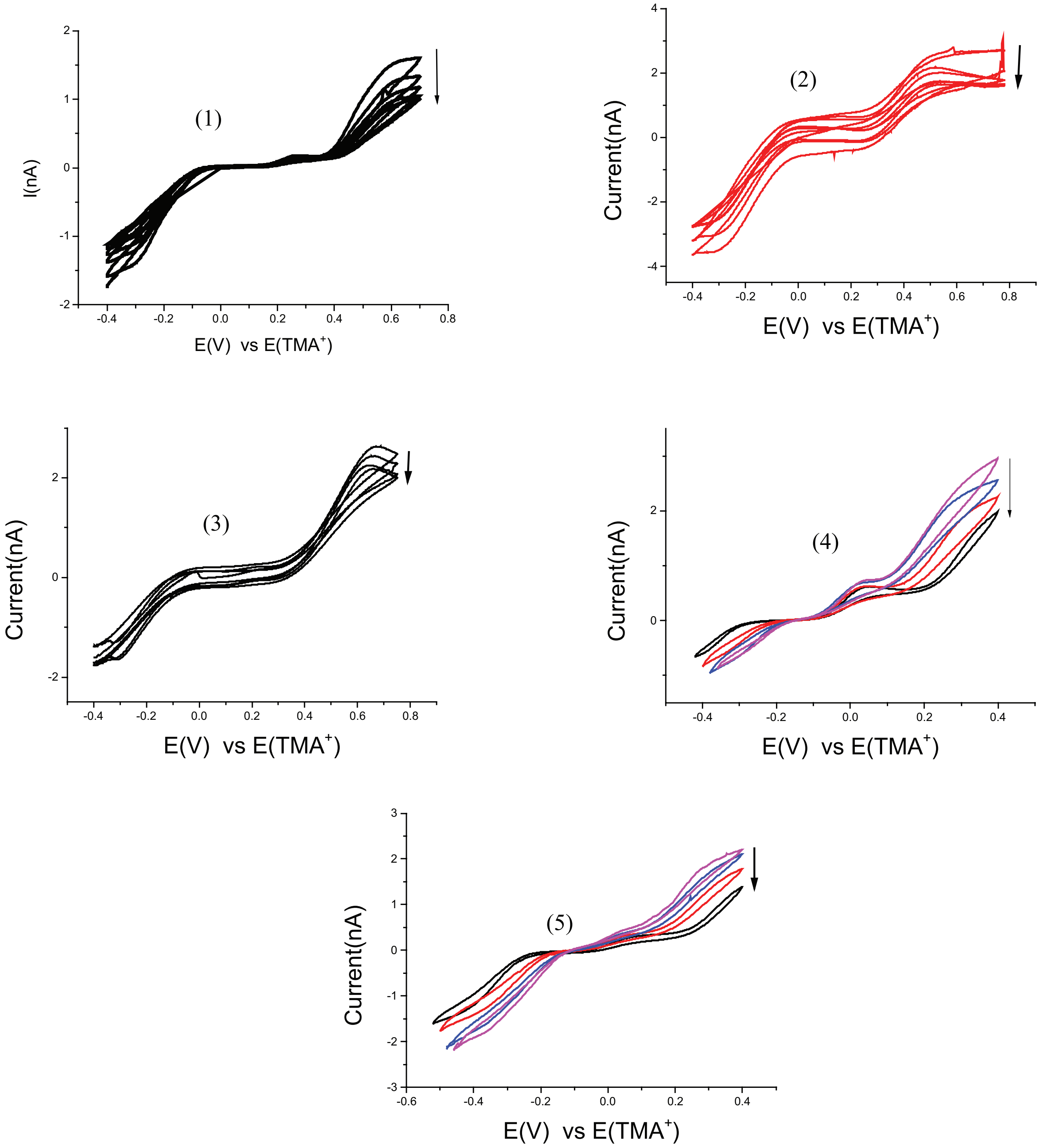

Fig. 8. The cyclic voltammetry of sulfate (1), perclorate (2), hydrogenphosphate (3), nitrate (4), carbonate and bromide (5) anions the scan rate changed from 100 to 10 mV/s (top to down for each figure).

The facilitated transfer peak of Ca^{2+} ion was observed at a sufficiently different potential values compared to that of Na^+. As a consequence, Ca^{2+} did not affect more the facilitated transfer peak of Na^+ ion which was used herein for its amperometric analysis. This situation can provide the way to analyze the facilitated transfer of Na^+ ion by PC in the presence of Ca^{2+} ion.