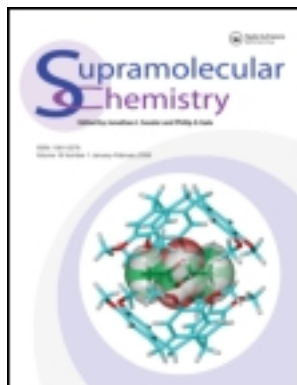


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### Synthesis and electrochemical properties of a novel calix[4]arene derivative for facilitated transfer of alkali metal ions across water/1,2-dichloroethane micro-interface

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## Synthesis and electrochemical properties of a novel calix[4]arene derivative for facilitated transfer of alkali metal ions across water/1,2-dichloroethane micro-interface

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The alkali metal ion transfers facilitated by a novel calix[4]arene derivative (OPEC) across the water/1,2-dichloroethane (1,2-DCE) micro-interface supported at the tip of a micropipette were presented. The well-defined voltammetric behaviours except  $\text{Cs}^+$  was obtained by cyclic voltammetry and differential pulse voltammetry. The bulk concentration of metal ions was much higher than that of OPEC in the performed measurements. The diffusion coefficient of OPEC in the 1,2-DCE phase was calculated as  $5.18 \pm 0.70 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . On the basis of the changes of the half-wave transfer potentials, the logarithms of the association constants having 1:1 ionophore–ion complex stoichiometry for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Rb}^+$  in 1,2-DCE were determined as 4.80, 4.62, 4.98 and 5.32, respectively. The facilitated ion transfers were also evaluated by the Randles equivalent circuit used for ac-impedance data analysis.

**Keywords:** facilitated ion transfer; micro-interface; steady-state cyclic voltammetry; calix[4]arene; alkali metal ions

### Introduction

Supramolecular chemistry is a branch of chemistry, especially linked with organic chemistry, which studies complex species formed from simple structures. Supramolecular chemistry is also referred by other names such as ‘host–guest chemistry’, ‘molecular recognition’ and ‘inclusion phenomena’ (1). Host–guest chemistry describes complexes that are composed of two or more molecules, or ions that are held together in unique structural relationships by a combination of hydrogen bonding, an ion pairing van der Waals force or forces other than those of full covalent bonds (2, 3). The molecular recognition can be inferred as a selective linkage between guest and host molecules, such as the crown ethers, cyclodextrins and calixarenes.

Calixarenes are obtained from the condensation reaction of formaldehyde with *p*-substituted phenols (4). They have vase-like structures including two rims that are the lower rim and the upper rim. The sizes of the rims affect the complexation properties of calixarenes (5). In addition to this influence, the nature of the groups attached, the number of donor atoms and their conformations are the other important effects that influence complexation properties of calixarenes. The easy and selective derivatisations from the upper or the lower rim and from both of the two rims have much attention on the host–guest recognition with wide applicability, such as in complexation chemistry (6), molecular catalysis (7), charge transfer (8) and chemical sensors (9, 10).

To investigate the charge transfer across the interface between two immiscible electrolyte solutions (ITIES), the electrochemical techniques are taken into account as a useful tool. Due to the use of organic solvents having low permittivity, such as 1,2-dichloroethane (1,2-DCE), the solution resistance of such organic phases must be compensated when working at large interfaces. In addition, miniaturisation of ITIES to micrometer-sized interfaces (micro-ITIES) annihilates this requirement so that it becomes easy to study reversible ion transfer reactions at micro-ITIES supported at the micropipette tip in comparison with centimetre-sized interfaces (macro-ITIES). Taylor and Girault (11) reported first micro-ITIES supported at the tip of a pulled glass micropipette. Afterwards, the determination of the ionic species limiting the potential window using the micropipette was investigated by Stewart et al. (12). Also different groups reported the transfer of alkali metal ions facilitated by crown ether (13), fullerene (14) and calix[4]arenes (15–20) across the water/1,2-DCE micro-interface supported at the tip of a micropipette.

This paper deals with the facilitated transfer of alkali metal ions across the water/1,2-DCE micro-interface by a novel calix[4]arene derivative (OPEC) firstly synthesised by our group. The interactions between alkali metal cations and ionophore were investigated by cyclic voltammetry, differential pulse voltammetry and ac-impedance measurements. The results showed that the facilitated ion transfers follow the transfer by interfacial

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complexation (TIC) and transfer by interfacial dissociation (TID) mechanism. The thermodynamic parameters of the obtained transfers were evaluated.

## Experimental

### Chemicals and instrumentation

All reagents were of analytical reagent grade. 1,2-DCE (Merck, Darmstadt, Germany, min. 99.5% G. C. Grade) was employed as an organic solvent in all electrochemical experiments. Ultrapure water was freshly obtained from Milli-Q system (Millipore) with a resistivity of 18.2 MΩ cm (at 25°C) to prepare aqueous solutions. Both of the solvents used in the cell were mutually saturated before experimentation. Bis(triphenylphosphoranylidene) ammonium tetrakis-(4-chlorophenyl) borate (BTTPATPBCl) was synthesised by the metathesis of BTPPACl (Fluka, Buchs, Germany) and KTPBCl (Lancaster Synthesis, Ward Hill, MA, USA) as the supporting electrolyte for an organic phase.

The micropipettes were obtained from a capillary glass tube by using Model P-1000 puller (Sutter Instrument Co., CA, USA). Motic AE21 inverted-trinocular microscope 100 × – 400 × (Motic Instruments, Xiamen, China) was used to inspect the shape and radii of the obtained micropipettes before each measurement. The electrochemical measurements, cyclic voltammetry, differential pulse voltammetry and ac-impedance were recorded by using IVIUM CompactStat (Ivium Technologies, Eindhoven, The Netherlands) combined with BAS C3 electrochemical cell stand.

### Synthesis of OPEC

The ionophore, 5,11,17,23-tetra-tert-butyl-25,26,27-tri-2-oxy-1-(4-phenoxyphenyl)ethanone-28-hydroxy calix[4]arene coded as OPEC, which was firstly synthesised by using the following procedure (21), is shown in Figure 1. A slurry

of 1 (2 mmol), K<sub>2</sub>CO<sub>3</sub> (8.8 mmol) and the alkylation agent (8.8 mmol) in acetonitrile (80 ml) was sonicated in an ultrasonic cleaning bath (40 KHz) at 60°C. After 18 h, the solvent was removed and water was added to the residue when a white solid precipitated. The mixture was acidified with 1 N HCl, and the compound was filtered. The solid was washed with water and dried in air. Crystallisation using CHCl<sub>3</sub>/MeOH yielded the trialkylated product. Its structure was confirmed by elemental analysis, FT-IR and <sup>1</sup>H NMR. Yield: 58%; yellow solid; mp 129–132°C; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>): 7.96 (s, 1H, ArOH), 7.65 (d, 6H, ArH), 7.33 (t, 3H, ArH), 7.00–7.30 (m, 8H, ArH), 6.95 (d, 6H, ArH), 6.88 (d, 12H, ArH), 5.23 (s, 6H, –OCH<sub>2</sub>CO), 4.33 (d, 4H, Ar–CH<sub>2</sub>–Ar), 3.38 (d, 4H, Ar–CH<sub>2</sub>–Ar), 1.17 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.10 (s, 27H, –C(CH<sub>3</sub>)<sub>3</sub>).

To obtain the standard partition coefficient (log *P*<sub>1,2-DCE</sub>) of OPEC between water and 1,2-DCE, we used ALOGPS (22) software and the methodology of Steyaert et al. (23). Consequently, the value of log *P*<sub>1,2-DCE</sub> was obtained as 9.14. This value indicates that OPEC is much more soluble in organic phase than in aqueous phase.

### Preparation of micropipettes

As the capillary glass tube, we selected borosilicate glass capillary (ID = 0.58 mm, OD = 1 mm) purchased from Sutter Instrument Co. (CA, USA) The tip of the micropipette was adjusted by changing the puller's five parameters (heat, filament, velocity, delay and pull). Also, to minimise the resistive potential drop, a pulling program was developed to produce short (patch-type) pipettes as emphasised in the literature (20,24). The inner diameter of the obtained micropipette was measured as approximately 3 μm. The outer wall was silanised to make it hydrophobic for flat interface by immersing in a solution of trimethylchlorosilane for about 5 min, while nitrogen gas was passing through the micropipette from the back. After drying, the silanised

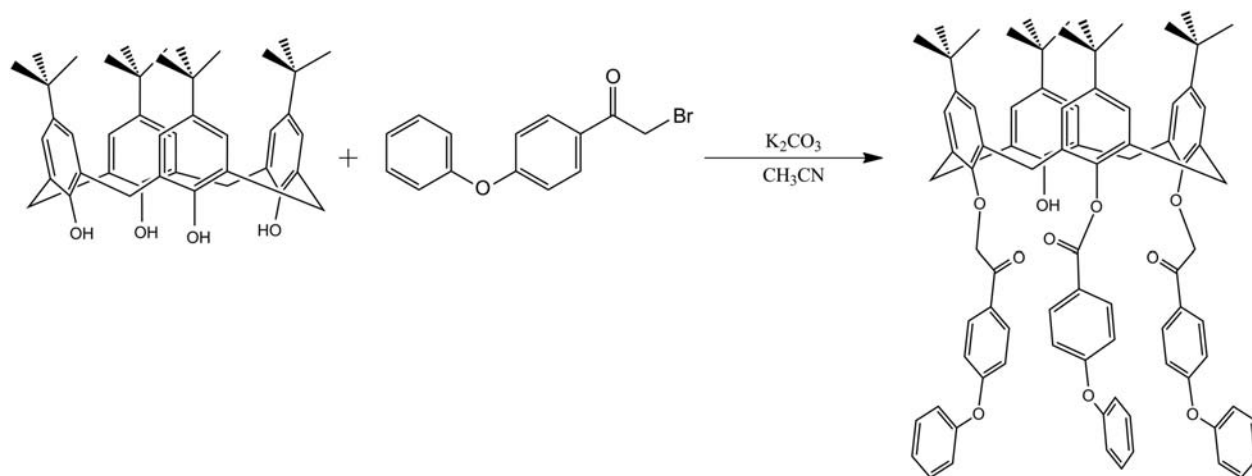


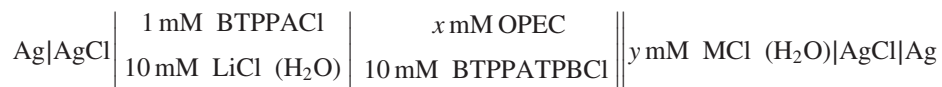
Figure 1. Synthesis of OPEC.

micropipettes were filled with the desired aqueous solution from the back using a small syringe (10  $\mu$ l).

### Electrochemical cell and measurements

The measurements were performed by the experimental set-up having three electrodes. The cell was made of borosilicate glass which was provided with a Luggin capillary probe as seen in Figure 2. The distance between the micropipette's tip and the organic reference solution was set as small as possible to minimise IR drop.

assumption' was used. The formal transfer potential of tetraethyl ammonium ( $\text{TEA}^+$ ) at a water/1,2-DCE interface can be estimated as 0.040 V on this scale (25). Therefore, the Galvani potential of  $\text{TEA}^+$  transfer was set as 0.040 V, and this scale was the basis for the current–voltage curves. All experiments were carried out at room temperature ( $23 \pm 1^\circ\text{C}$ ). The electrochemical cell for the facilitated transfer of alkali metal ions by OPEC can be represented as follows:



Cell 1

The platinum wire in organic phase was used as counter electrode. Ag/AgCl wires in water and reference-aqueous phase prepared from very thin Ag wire by using a method described in the literature (18) were used as working and reference electrodes, respectively. To calibrate the transfer potential, the 'Tetraphenylarsonium tetraphenylborate (TATB)

where the interface polarised by the application of the potential difference is indicated by the double bar, and the variables  $x$  and  $y$  represent the bulk concentrations of ionophore and metal ions added to 1,2-DCE and aqueous phases, respectively. The scan rate was adjusted to  $50 \text{ mV s}^{-1}$  for the cyclic voltammetry experiments. The potential step, the pulse amplitude and the pulse time were

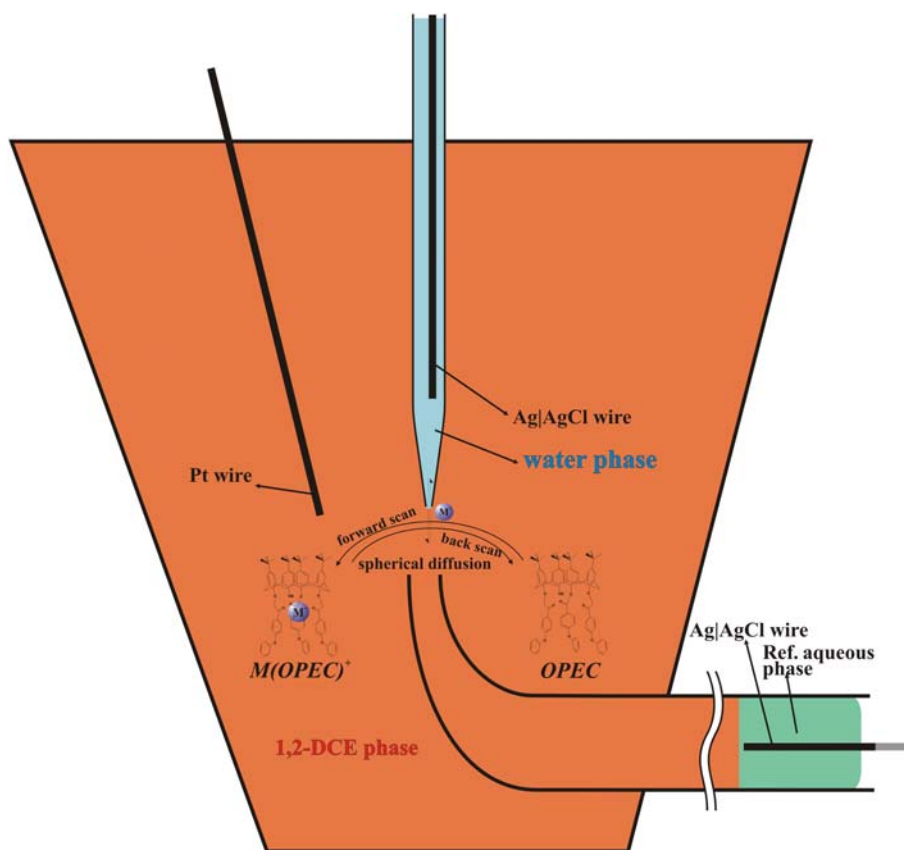


Figure 2. Schematic presentation of the cell design and the facilitated transfer of  $M^+$  by OPEC.

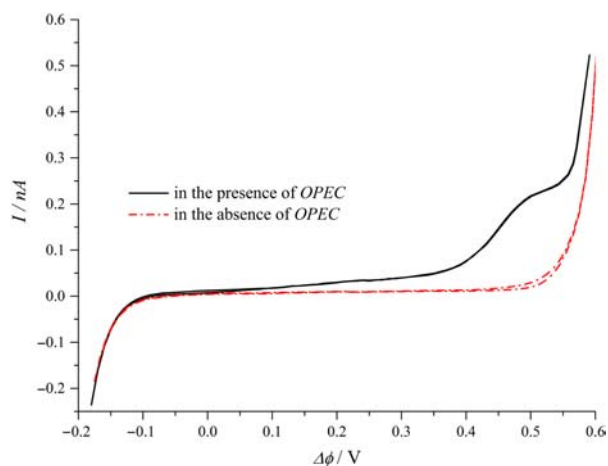


Figure 3. The cyclic voltammograms for  $\text{Li}^+$  ion transfer non-facilitated and facilitated by OPEC. The ionophore concentrations ( $x$ ) for the dotted and solid lines are 0 and 0.75 mM in Cell 1 ( $y = 100$  mM), respectively.

10 mV, 60 mV and 80 ms for the differential pulse voltammetry experiments, respectively.

## Results and discussion

### Characterisations of the facilitated ion transfers

Figure 3 shows the obtained voltammograms of the transfer of  $\text{Li}^+$  ion in the absence (dashed line) and presence (solid line) of OPEC in the 1,2-DCE phase using

Cell 1. In both cases, the potential window is limited by the transfer of alkali metal ion (here  $\text{Li}^+$ ) at the positive value and by the transfer of  $\text{Cl}^-$  ion at the negative value from the aqueous phase to the organic phase. It can be obviously seen in Figure 3 that there is no ion transfer in the potential window in the absence of OPEC in the organic phase. In contrast, in the presence of OPEC, the facilitated transfer of  $\text{Li}^+$  ion is observed from the aqueous to the organic phase.

According to the voltammogram shape of the facilitated transfer of  $\text{Li}^+$  ion, when the metal ion concentration is much higher than that of OPEC ( $c_{\text{Li}^+} \gg c_L$ ) in Cell 1, we can infer that the rate-determining step (rds) in this procedure is the spherical diffusion of OPEC from the bulk 1,2-DCE solution to the interface following TIC mechanism. For the reverse scan, the process is dominated by the same diffusion manner of the metal complex of OPEC according to TID mechanism as shown in Figure 2. Or else, a peak-shape voltammogram is observed if any species transfers from inside of the micropipette to outside (26).

Figure 4 shows the obtained steady-state cyclic voltammograms for the facilitated transfer of alkali metal ions when the concentration of the metal ion in the aqueous phase is much higher than the concentration of OPEC in the 1,2-DCE phase (0.75 mM). The chloride solutions of the respective metals ions (100 mM) were used in the aqueous phase. The semi-logarithmic relationships between the Galvani potential difference

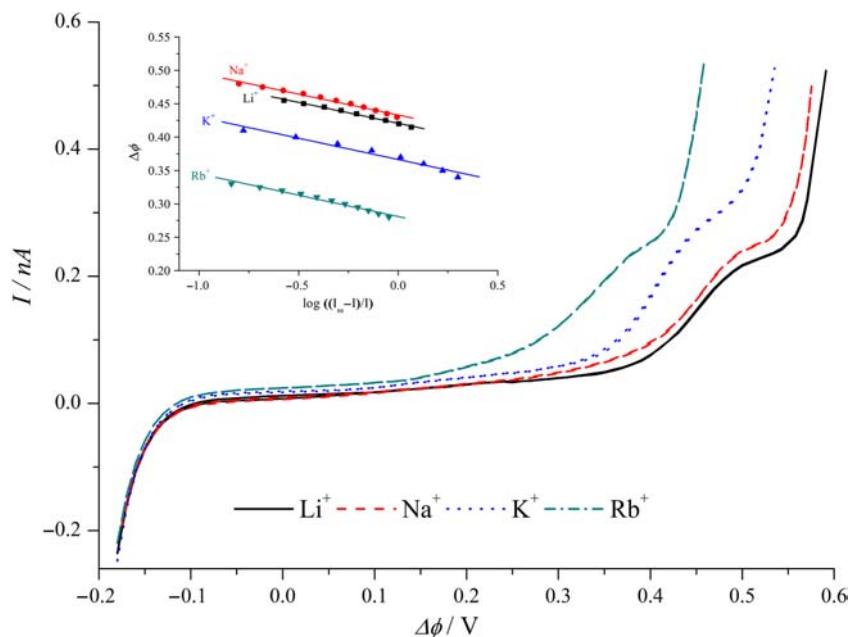


Figure 4. The steady-state cyclic voltammograms of the facilitated transfers of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Rb}^+$  by OPEC across the water/1,2-DCE micro-interface in Cell 1 ( $x = 0.75$ ,  $y = 100$ ). The inset shows the relationships between the Galvani potential difference of the transfers and  $\log [(I_{\text{ss}} - I)/I]$ ; the micropipette diameter is 3  $\mu\text{m}$ .

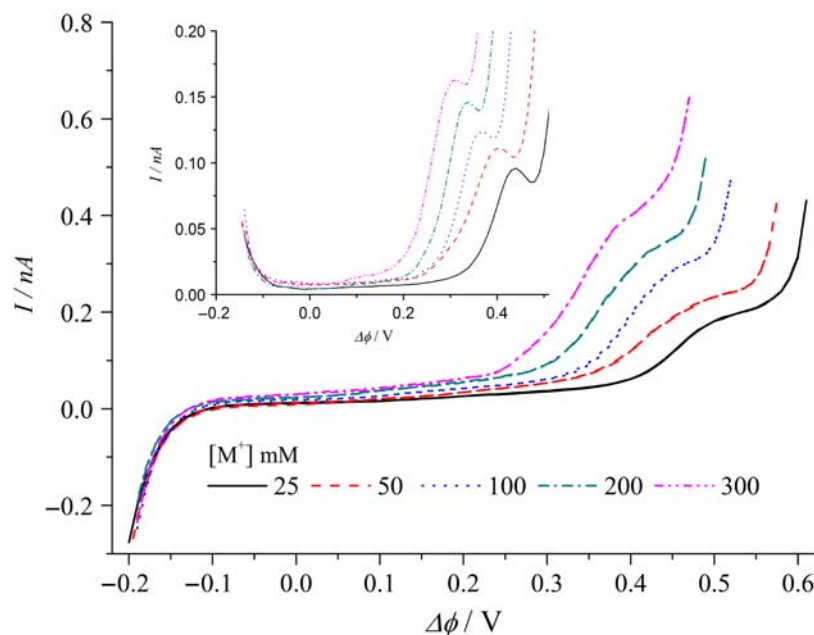


Figure 5. The obtained steady-state cyclic voltammograms and the differential pulse voltammograms (inset) of  $K^+$  ion transfer facilitated by OPEC across the water/1,2-DCE interface at various metal concentrations ( $x = 0.75$ ,  $y = 25-50-100-200-300$ ).

and  $\log[(I_{ss} - I)/I]$  are linear with slopes of 62.5, 62.7, 63.7 and  $64.2 \text{ mV dec}^{-1}$  for  $Li^+$ ,  $Na^+$ ,  $K^+$  and  $Rb^+$ , respectively (the inset in Figure 4). The values are in agreement with those in the literature for a univalent ion (26,27). They also indicate that the processes of the facilitated transfers have reversible nature.

#### Determination of association constants

Alkali metal ions are quite hydrophilic in aqueous solution, therefore, their unassisted transfer from aqueous to organic phase is hard to observe. Hence, hydrophobic ionophores that dissolve in the organic phase can be used to obtain their facilitated transfer in the potential window. The main purpose is to achieve the lower Gibbs energy of ion transfer. In this situation, the complexation reaction between metal ion and hydrophilic ionophore across the polarised interface can be described by the following equation:



where  $n$  represents the stoichiometry of the complex. For the facilitated transfer reaction, the association constant,  $\beta$ , is defined as given in Equation (2).

$$\beta = \frac{[ML_n^+]}{[M^+][L]^n} \quad (2)$$

When the concentration of the metal ion in the aqueous phase was much higher than the concentration of the hydrophobic ionophore in the organic phase, Su et al. (28) pointed out for a TIC that the value of association constant

for a 1:1 complexation can be determined by the evaluation of the half-wave Galvani potential ( $\Delta_o^w \phi_{M^{z+}}^{1/2}$ ) from cyclic voltammogram as given in Equation (3).

$$\Delta_o^w \phi_{M^{z+}}^{1/2} = \Delta_o^w \phi_{M^{z+}}^{0'} + \frac{RT}{zF} \ln \frac{D_L}{D_{ML^+}} - \frac{RT}{zF} \ln(\beta_1^0 c_{M^{z+}}^w) \quad (3)$$

where  $\beta_1^0$  is the association constant of the complex in the organic phase,  $\Delta_o^w \phi_{M^{z+}}^{0'}$  is the formal transfer potential of the free metal ion and  $c_{M^{z+}}^w$  is the initial concentration of the metal ion in the water phase. To determine the association constants between the alkali metal ions and OPEC, the

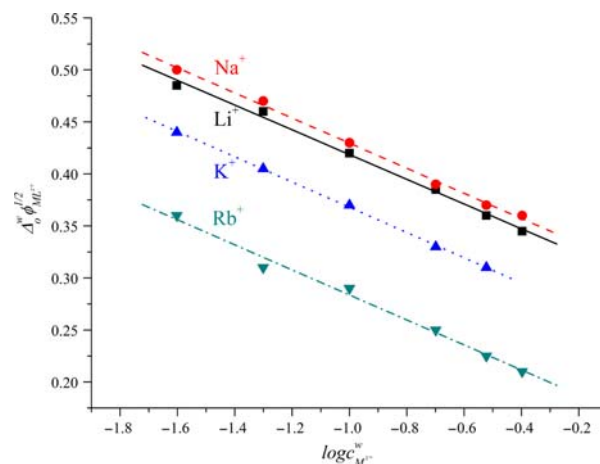


Figure 6. Dependence of the half-wave transfer potentials on the logarithm of the concentration of alkali metal ions in water phase.

Table 1. Thermodynamic parameters of alkali metal ions transfer assisted by OPEC across the micro-interface between water and 1,2-DCE.

Ions	$\Delta_o^w \phi_{M^{z+}}^{0/}$ (V) (27)	$\Delta_o^w \phi_{M^{z+}}^{1/2}$ * (V)	$\Delta \Delta_o^w G^{0/**}$ (kJ mol <sup>-1</sup> )	Slope	s	log $\beta_1^0$
Li <sup>+</sup>	0.576	0.420	-15.1	-123	1:1	4.80
Na <sup>+</sup>	0.579	0.430	-14.4	-120	1:1	4.62
K <sup>+</sup>	0.538	0.370	-16.2	-121	1:1	4.98
Rb <sup>+</sup>	0.475	0.290	-17.9	-120	1:1	5.32

Notes: \* The half-wave transfer potentials were determined under experimental conditions;  $y = 100$  mM,  $x = 0.75$  mM and  $v = 50$  mV s<sup>-1</sup>. \*\*  $\Delta \Delta_o^w G^{0/**} = -nF(\Delta_o^w \phi_{M^{z+}}^{0/} - \Delta_o^w \phi_{M^{z+}}^{1/2})$  is the driving force of the assisted ion transfer under the experimental conditions (26).

studies of concentration dependence on the half-wave potentials were carried out for each metal ion. The obtained steady-state cyclic voltammograms and the differential pulse voltammograms (the inset) for the K<sup>+</sup> ion transfer facilitated by OPEC under various metal ion concentrations are shown in Figure 5. It is clearly seen that the half-wave potential shifts negatively with the increasing concentration of metal ions verifying Equation (3).

Figure 6 depicts the relationships between the logarithms of the concentration (log  $c_{M^{z+}}$ ) of the metal ions and  $\Delta_o^w \phi_{M^{z+}}^{1/2}$  obtained from the steady-state cyclic voltammograms. Linear relationships were observed with the slopes of 120–123 mV dec<sup>-1</sup>. The slopes are close to the theoretical value for monovalent reversible transfer at 20°C (118 mV dec<sup>-1</sup>), indicating that stoichiometric ratio is 1:1 (26) for all metal ion transfers. By using Equation (3), the association constants calculated by the intercepts are given in Table 1.

The association constants of the complexes occurring between various calixarene derivatives and alkali metal ions in related papers are also given in Table 2. As can be seen, OPEC has moderate values of the association constants according to the indicated literature.

### Effect of the concentration of OPEC

When the concentration of metal ion in aqueous phase is in excess, the limiting current is proportional to the concentration of the ionophore. Therefore, across the water/1,2-DCE micro-interface supported at a micropipette tip, the equation for the steady-state current ( $I_{ss}$ ) of the facilitated ion transfer

by an ionophore can be written as (30)

$$I_{ss} = AzFD_i c_i r, \quad (4)$$

where  $z$  is the charge number of the transferring complexes,  $F$  is Faraday's constant,  $D_i$  is the diffusion coefficient of the ionophore,  $c_i$  is an initial concentration of ionophore and  $r$  is the radius of the micropipette,  $A$  is a special parameter that is used to adjust the effect of the back diffusion contribution of the electrodes, and also the effect of the shape and silanisation condition of the micropipette. Its value was determined as 4.64 for our experimental conditions (30,31).

Figure 7 shows the facilitated transfers of Li<sup>+</sup> ion at different concentrations of OPEC across the water/1,2-DCE micro-interface. As can be seen, although the half-wave transfer potentials have not changed significantly, the steady-state currents of the facilitated transfer increase with the bulk concentration of OPEC. This result supports that the facilitated ion transfer is limited by the spherical diffusion of OPEC across the water/1,2-DCE micro-interface from organic phase. Also, no change at the half-wave transfer potential with the changing in concentration of OPEC confirms that the facilitated transfers occur with the complexation having 1:1 stoichiometry according to Equation (3).

The inset in Figure 7 depicts that the steady state currents are proportional to OPEC concentration as emphasised in Equation (4). The linear graphs were analysed for each facilitated transfer, and the diffusion coefficient of OPEC in 1,2-DCE phase was calculated averagely as  $(5.18 \pm 0.70) \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>, which is in harmony with experimentally reported values for diffusion coefficients of calixarenes (16,20).

Table 2. The comparison of the obtained association constants for the transfer of alkali metal ions across the water/1,2-DCE micro-interface with the published data.

Logarithm of association constants (log $\beta_1^0$ )				
Ions				
Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Ref.
4.80	4.62	4.98	5.32	Present study
3.94	4.01	5.01	4.68	(20)
11.6	13.0	11.3	9.2	(16)
–	3.99	–	–	(29)

### ac-impedance measurements

The ac-impedance experiments were carried out at the frequency range between 100 kHz and 500 Hz for Cell 1 ( $x = 0.75$  mM;  $y = 100$  mM). The frequency range could not be extended to lower frequencies due to the effect stemming from the vibration of the tip. Figure 8 shows the complex-plane impedance plots at the half-wave potentials of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Rb<sup>+</sup> transfers facilitated by OPEC.

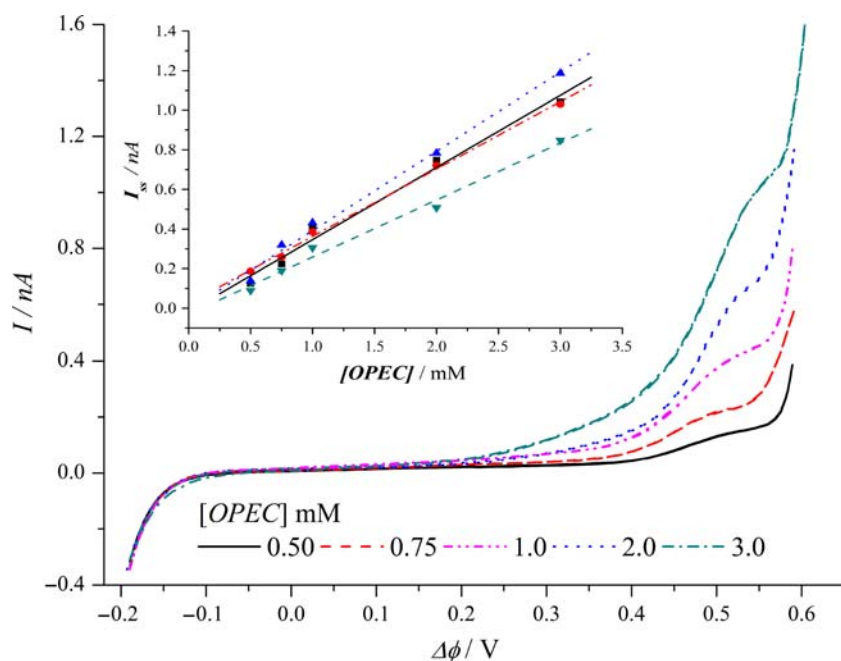


Figure 7. Cyclic voltammograms for  $\text{Li}^+$  ion transfer across the water/1,2-DCE interface at various concentrations of OPEC in 1,2-DCE phase. The inset shows the changes of steady-state currents of transfers upon the concentration of OPEC in 1,2-DCE phase: the micropipette diameter is  $3 \mu\text{m}$  and the scan rate is  $50 \text{ mV s}^{-1}$ .

In this frequency range, the cell exhibits the behaviour of the Randles-type equivalent circuit. The lack of a full semicircle can be attributed to the contributions of kinetic and diffusional processes to the impedance overlap as the ion transfer is a fast process (32).

The obtained experimental results were analysed by fitting to Randles-type circuit consisting of the solution resistance ( $R_s$ ) in series with the parallel combination of the interfacial capacitance ( $C_{dl}$ ), the kinetic resistance ( $R_{ct}$ ) and the faradaic impedance of the ion transfer ( $Z_{\text{CPE}}$ ). The obtained impedance values of the facilitated ion

transfer were used to determine the relationship between the capacitance and the corresponding frequency taking into account Equation (5) (33).

$$Z_{\text{CPE}} = \frac{1}{Y_0} (i\omega)^{-n}, \quad (5)$$

where  $Y_0$ ,  $n$  and  $\omega$  represent the admittance coefficient, the exponent and the frequency, respectively. Figure 9 shows the linear relationships between the logarithms of the impedances and the frequencies for each facilitated

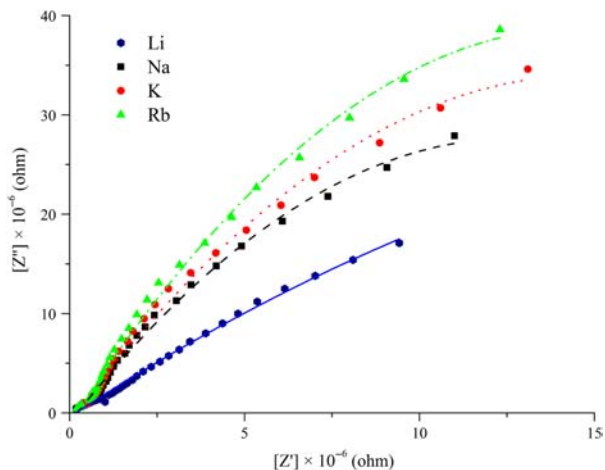


Figure 8. The complex-plane impedance plots of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Rb}^+$  transfers facilitated by OPEC for Cell 1, fitted to the Randles-type equivalent circuit ( $x = 0.75 \text{ mM}$ ,  $y = 100 \text{ mM}$ ).

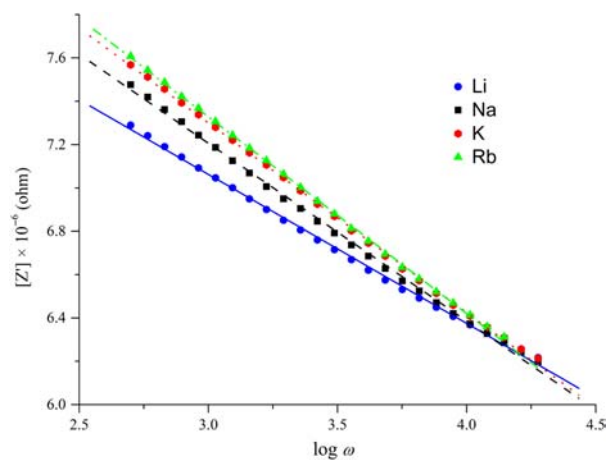


Figure 9. The plots of linear relationships of logarithm of frequency versus logarithm of the obtained impedance for the facilitated transfer of alkali metal ions by OPEC.



Table 3. The obtained data of the elements are according to the equivalent circuit that is fitted to Figure 8.

Ions	$Y_0 \times 10^{10} (\Omega^{-1} s^n)$	$n$
Li <sup>+</sup>	7.46	-0.69
Na <sup>+</sup>	2.15	-0.82
K <sup>+</sup>	1.18	-0.88
Rb <sup>+</sup>	0.89	-0.91

transfer of alkali metal ions by OPEC. The fit values are tabulated in Table 3.

As can be seen in Table 3, the exponent ( $n$ ) values are higher than the expected value 0.5 indicating that the constant phase impedances exhibit different characteristic properties from Warburg impedance. This difference was attributed to the spherical diffusion occurring at micro-interface as different from linear diffusion, which is generally a validity of Warburg impedance (34,35). The present of spherical diffusion at the micro-interface indicates that the facilitated ion transfer is controlled by the diffusion of OPEC in organic phase. On the other hand, the results confirmed that the facilitated transfers occur according to the TIC/TID mechanism.

### Conclusion

In this work, we studied the electrochemical behaviour of the transfer of alkali metal ions facilitated by OPEC across the water/1,2-DCE micro-interface. The results of cyclic voltammograms and ac-impedances obtained for these processes confirm that the facilitated transfers follow TIC and TID mechanism. These results show that OPEC is a good ionophore for recognition of used ions, and voltammetry is an efficient way to investigate the ionic recognition ability of this kind of compound at the micro-interface of two immiscible electrolyte solutions. The selectivity of OPEC towards alkali ions follows the sequence  $Rb^+ > K^+ > Li^+ > Na^+$ . In the voltammetric polarisation window, rather poor steady-state voltammograms of facilitated Cs<sup>+</sup> transfer were observed when the concentration of Cs<sup>+</sup> varied from 0.025 to 0.3 M. This made the quantitative analysis quite difficult or impossible.

### Acknowledgements

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