

Voltammetric Studies of Anion Transfer Reactions Across a Microhole Array-Water/PVC-NPOE Gel Interface

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Voltammetric characterization of hydrophilic anion transfer processes across a 66 microhole array interface between the water and polyvinylchloride-2-nitrophenyloctylether gel layer is demonstrated. Since the transfer of hydrophilic anions including Br^- , NO_3^- , I^- , SCN^- and ClO_4^- across the liquid/gel interface usually sets the potential window within a negative potential region, a highly hydrophobic organic electrolyte, tetraoctylammonium tetrakis(pentafluorophenyl)borate, providing a wider potential window was incorporated into the gel phase. The transfer reaction of perchlorate anions across the microhole-water/gel interface was first studied using cyclic voltammetry and differential pulse voltammetry. The full voltammetric response of perchlorate anion transfer was then used as a reference for evaluating the half-wave transfer potentials, the formal transfer potentials and the formal Gibbs transfer energies of more hydrophilic anions such as Br^- , NO_3^- , I^- and SCN^- . The current response associated with the perchlorate anion transfer across the micro-water/gel interface versus the perchlorate concentration was also demonstrated for sensing applications.

Key Words : Anion transfer, Micro-liquid/gel interface, Formal Gibbs transfer energy, Perchlorate anion, Amperometric sensor

Introduction

Ion transfer reactions across an interface between two immiscible electrolyte solutions (ITIES) have gained considerable interests due to their significant importance in biomimetic studies of ion transfer across cellular membranes in the living cells in addition to a wide applicability in amperometric ion sensing, drug uptake studies, extraction chemistry, energy storage and conversion and other fields.¹⁻⁶ Various electrochemical methods in conjunction with different experimental set-ups such as two-phase electrode systems, three-phase junctions, and four-electrode systems have been implemented to understand the kinetics and thermodynamics of various organic and inorganic ion transfer reactions at the ITIES.⁷⁻⁹ In addition, the use of currents associated with ion transfer reactions across the ITIES as a function of ionic species concentration have extensively been investigated for ion sensing applications.^{10,11}

In order to utilize the ITIES for the practical ion sensing, extensive steps have been taken to reduce the size of interface to micrometer range such as a microhole, an array of microholes and a micropipette tip which improved the uncompensated ohmic loss caused by both a highly resistive organic phase and a large interface area.¹⁰⁻¹⁴ The mechanical instability of immiscible liquid/liquid interface was also tackled by introducing a liquid/gel interface *via* the gelification of one of the phases utilizing polymers.¹⁵ Such a micro-liquid/gel interface has successfully been implemented as an effective and sensitive detection platform of various

cationic species,¹⁰ heavy metals,¹⁵ as well as enzymatic products.¹⁶⁻¹⁸

Despite of extensive efforts made on creating ion selective and sensitive sensing platforms over the last decade, there have only been few reports that employ the liquid/liquid interface for studying hydrophilic anion transfer and their sensing applicabilities.^{2,19} This is probably due to the fact that 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.^{2,20} The use of a highly hydrophobic organic salt involving a hydrophobic cation as an organic supporting electrolyte in the organic phase can provide a wider potential window at the negative end and thus assist in elucidating the transfer reaction of anions across the ITIES. For example, the transfer reactions of I^- , Br^- and Cl^- anions across the interface between the water and an ionic liquid containing a very hydrophobic supporting electrolyte have been reported.²¹

In this paper, the transfer reaction of anions across a 66 microhole array interface between an aqueous and a PVC-NPOE gel phase is described utilizing tetraoctylammonium tetrakis(pentafluorophenyl)borate (TOATB) salt as an organic supporting electrolyte in the gel layer. The TOA^+ ion, having a relatively higher Gibbs energy of transfer (ΔG_{T}^0) provides an extended potential window at the negative end and therefore provides a way to investigate the characteristics of interfacial transfer reactions of hydrophilic

anion species across the interface within the accessible potential window.²¹ Cyclic voltammetry was first employed to characterize the transfer process of Br^- , NO_3^- , I^- , SCN^- and ClO_4^- anions across the polarized micro-liquid/gel interface with an internal reference, tetramethylammonium (TMA^+) ion. The half-wave transfer potential, the formal transfer potential and the formal Gibbs transfer energy of each anion were then evaluated based on their voltammetric responses. In order to demonstrate the aqueous/gel micro-hole array interface described above as an anion sensitive platform, perchlorate anion transfer reaction was chosen due to its relatively lower Gibbs energy of transfer from aqueous to organic phase in addition to the relatively high diffusion coefficient in water ($D_{\text{ClO}_4^-}$ in water = $1.27 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$).²² Moreover, the detection of perchlorate anions is of great importance since the contamination in drinking water is now considered as an emerging threat for human health and environment²³ and thus the Environmental Protection Agency (EPA) proposed a permit level in drinking water of 15 ppb (157 nM).²⁴ The current responses associated with the transfer of perchlorate ions across the micro-water/PVC-gel interface as a function of the perchlorate ion concentration were evaluated using cyclic voltammetry and differential pulse stripping voltammetry.

Experimental

Chemicals. Polyvinylchloride (PVC, high molecular weight, Sigma-Aldrich), 2-nitrophenyloctylether (NPOE, Fluka), lithium chloride (LiCl, Fluka), sodium chloride (NaCl, Merck), potassium chloride (KCl, Merck), tetramethylammonium chloride (TMACl, > 97%, Sigma-Aldrich), sodium sulfate (Na_2SO_4 , Shinyo Pure Chem. Ind. Ltd.), sodium acetate (CH_3COONa , Sigma-Aldrich), sodium bicarbonate (NaHCO_3 , Sigma-Aldrich), sodium nitrite (NaNO_2 , Sigma-Aldrich), sodium bromide (NaBr, Sigma-Aldrich), sodium nitrate (NaNO_3 , Sigma-Aldrich), sodium iodide (NaI, Sigma-Aldrich), sodium thiocyanate (NaSCN , Sigma-Aldrich), sodium perchlorate (NaClO_4 , Sigma-Aldrich), lithium tetrakis(pentafluorophenyl)borate etherate (LiTB, Boulder Scientific Company), tetraoctylammonium bromide (TOABr, Fluka), tetraoctylammonium chloride (TOACl, Sigma-Aldrich) were all used as received. The organic phase supporting electrolyte, tetraoctylammonium tetrakis(pentafluorophenyl)borate (TOA^+TB^-) was prepared by metathesis 1:1 of tetraoctylammonium bromide (TOABr) and lithium tetrakis(pentafluorophenyl)borate etherate (LiTB) in methanol-water (V:V = 2:1) mixtures. The resulting precipitates were separated from the reaction mixtures by filtration followed by the several times washing with Millipore-filtered water. The

solvent was then evaporated using a vacuum dryer at 100 °C overnight. All aqueous solutions were prepared using Millipore-filtered water.

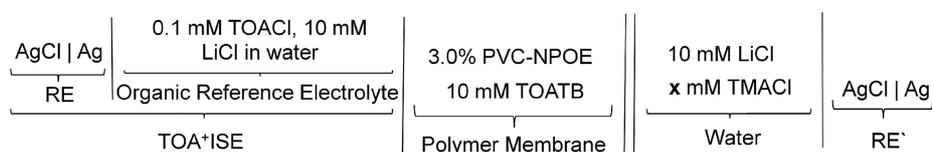
Fabrication of Micro-Liquid/Gel Interface. A 66 (11×6) microhole array interface was first created by drilling the supporting film of a polyethylene terephthalate film (PET, 12 μm thick, Melinex type 'S' from ICI Films, UK) using a UV Excimer laser according to the procedure described elsewhere.¹⁴ The diameter of each microhole was estimated as 22 μm and 13 μm for entrance and exit side, respectively. The PVC-NPOE mixture solution was prepared by dissolving PVC (3% w/w) and 10 mM TOATB in NPOE followed by heating the solution mixture at about 120 °C for 30 minutes. Twelve microliters of the PVC-NPOE mixture heated at 80 °C was finally casted on the exit side of the 66 microhole array of PET film and kept for minimum 6 hours at room temperature to be gelified and contacted with aqueous phase to form an array of microhole-liquid/gel interface.

Electrochemical Measurements. All electrochemical experiments were conducted in a two electrode mode using a computer-controlled potentiostat (Autolab PGSTAT30 Ecochemie) without any IR drop compensation. Two Ag/AgCl electrodes were used for the aqueous and organic gel phase, respectively. General Purpose Electrochemical System (GPES) software v.4.9 was used to acquire and analyze all electrochemical data. All experiments were carried out at room temperature and sweep rate for cyclic voltammetry experiments was $20 \text{ mV} \cdot \text{s}^{-1}$ unless otherwise stated.

Results and Discussion

Characterization of Ion Transfer Reaction Across Micro-Water/PVC-NPOE Gel Interface Using TOATB Organic Supporting Electrolyte. The use of TOATB electrolyte in the organic gel phase for studying ion transfer reaction across the 66 microhole array-water/PVC-NPOE gel interface was first characterized utilizing the transfer of the reference ion, TMA^+ ion. The electrochemical response of ion transfer was investigated using cyclic voltammetry and the electrochemical cell set-up, Cell 1.

Cyclic voltammograms resulted from the transfer of various concentrations of TMA^+ ions from the aqueous to the organic gel phase are displayed in Figure 1. In the absence of TMA^+ ions ($x=0$ in Cell 1), the positive end of the potential window is set by the transfer of Li^+ or TB^- ions and the negative end is limited by the transfer of either TOA^+ or Cl^- ions across the polarized micro-water/gel interface (see Figure 1(i)). In the presence of TMA^+ ions, a steady-state voltammogram on the forward scan and a peak-shaped voltammogram on the reverse scan were observed for the



Cell 1

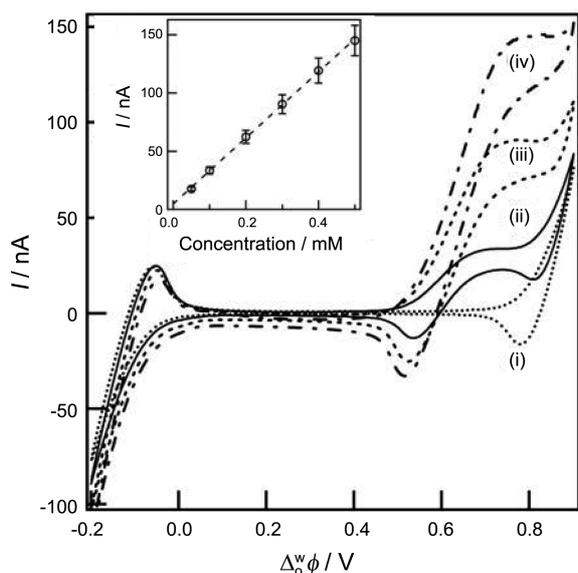


Figure 1. A series of cyclic voltammograms for different concentrations of TMA^+ ion transfer across a 66 microhole array interface between the aqueous and PVC-NPOE gel phases containing TOATB using Cell 1. 10 mM LiCl in (i) the absence of TMA^+ ion and in the presence of (ii) 0.1 mM, (iii) 0.3 mM and (iv) 0.5 mM TMA^+ ions. Scan rate = $20 \text{ mV}\cdot\text{s}^{-1}$. Inset shows a plot of the steady state current versus the TMA^+ ion concentration from 0.05 to 0.5 mM. Dotted line shows a linear fit.

direct transfer of TMA^+ ions within the available potential window. The steady-state response is due to the fact that a hemispherical diffusion flux as in the case of the microdisc dominates when the TMA^+ ion transfers from the aqueous to organic phase (ingress). On the other hand, the peak-shaped response when the TMA^+ ion transfers from the organic to aqueous phase (egress) is mainly originates from a linear diffusion flux due to the resistive holes filled with the gel.^{14,18} The steady-state current increases as a function of TMA^+ ion concentration with a linear slope $283.32 \text{ nA}\cdot\text{mM}^{-1}$ where the scan rate was kept as $20 \text{ mV}\cdot\text{s}^{-1}$. This value is in good agreement with the theoretical value ($280.19 \text{ nA}\cdot\text{mM}^{-1}$)¹⁴ calculated for a perfectly inlaid independent micro-disc interface using the Eq. (1):

$$I_{ss}^{w \rightarrow o} = 4nz_i F D^w c^w r \quad (1)$$

where n is the number of microholes, z_i is the charge number of ionic species, F is the Faraday constant, D^w is the diffusion coefficient, c^w is the concentration of ionic species in aqueous phase, r ($11 \mu\text{m}$) is the radius of microhole interface. This is a good indicator that the TOATB organic electrolyte can be employed for the study of ion transfer

reactions across the micro-water/PVC-NPOE gel interface.

We are now in a position to utilize the TOA^+ organic supporting cation electrolyte for the study of direct transfer of hydrophilic anions which offers wider potential window range at the negative potential compared to that of conventionally used cations such as tetrabutylammonium (TBA) or bis(triphenylphosphoranylidene) ammonium (BTTPA) cations. The transfer reaction of various anionic species such as Br^- , NO_3^- , I^- , SCN^- and ClO_4^- across the microhole-interface was characterized using cyclic voltammetry with Cell 2.

The study of thermodynamic properties and the typical lipophilicity ordering of the anion series are of great importance because of their biological activity and applicability in various research areas. Also, the lipophilicity of the anions is correlated to their thermodynamic properties, which leads to the different anionic species exhibiting different tendencies to transfer from the water to the organic phase. Therefore, the initial experiments performed were focused on estimating the thermodynamic parameters of ion transfer reactions including the half-wave potential, the formal transfer potential and the formal Gibbs energy of transfer of various hydrophilic anionic species in the presence of the well defined reference ion, tetramethylammonium (TMA^+) ion.

Figure 2 shows a series of cyclic voltammograms for the transfer of various anions across the polarized aqueous/

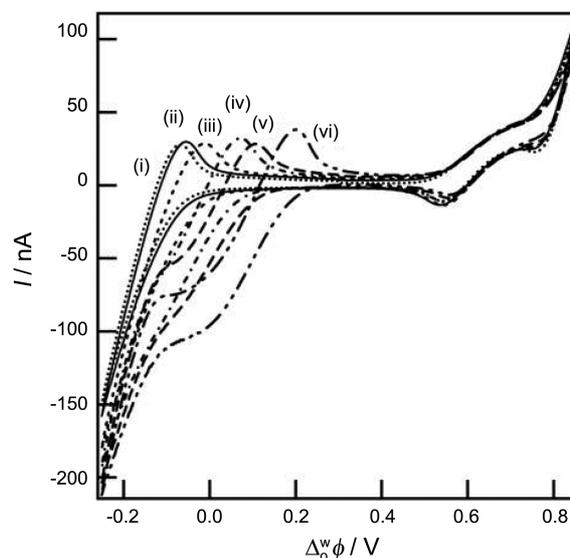
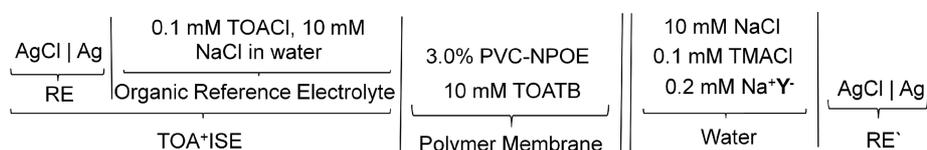


Figure 2. Cyclic voltammograms for the transfer process of various anionic species across the microhole-water/organic gel interface using Cell 2. (i) 10 mM NaCl and 0.1 mM of TMACl. (ii) 0.2 mM NaBr, (iii) 0.2 mM NaNO_3 , (iv) 0.2 mM NaI, (v) 0.2 mM NaSCN and (vi) 0.2 mM NaClO_4 in the presence of 0.1 mM of TMACl and 10 mM NaCl. Scan rate = $20 \text{ mV}\cdot\text{s}^{-1}$.



Cell 2

PVC-NPOE gel micro-interface using Cell 2. In the absence of other anionic species the potential window at the positive end was limited by either Na^+ or TB^- ion transfer, while the negative end was restricted by the transfer of chloride or TOA^+ ions. Therefore, anion transfer studies in this work were limited to the anions which are less hydrophilic than chloride in the Hofmeister series.²⁵ One of the conventional methods to determine the thermodynamic properties of an unknown ion transfer occurring across a polarized liquid/liquid interface is the use of standard thermodynamic values of well characterized reference ions⁷ such as TMA^+ . For example, the transfer characteristics of TMA^+ were utilized to estimate the thermodynamic properties of K^+ , Na^+ , NH_4^+ cation transfer across a liquid/gel interface in a previous study.¹⁰ Therefore, the TMA^+ ion was used as an internal reference in order to estimate the half-wave potential and the formal transfer potential values of hydrophilic anions in accordance with the TATB estimation using the following expression:¹⁰

$$\Delta_o^w \phi_{1/2, A^-} = \Delta_o^w \phi_{1/2, A^-} - [\Delta_o^w \phi_{1/2, \text{TMA}^+} - \Delta_o^w \phi_{\text{TMA}^+}^{\theta'}] \quad (2)$$

where, $\Delta_o^w \phi_{\text{TMA}^+}^{\theta'}$ is 125 mV.

It can be seen in Figure 2 is that the estimation of experimental half-wave potential for Br^- , NO_3^- and I^- anions appears to be more difficult than that of the perchlorate ion as the transfer of these anions occurs close to the negative end of the potential window. Thus the steady-state current responsible for these anion transfer processes from water to the organic gel layer was not clearly observed. The half-wave potential values for these anions were therefore estimated by the use of the half-wave potential for perchlorate ion transfer (Figure 2(vi)) as a reference. The half-wave potential as well as the current at the half-wave potential of perchlorate transfer ($\Delta_o^w \phi_{1/2, \text{ClO}_4^-}$) with respect to TMA^+ ion transfer ($I_{1/2, \text{ClO}_4^-}$) were first measured from the voltammetric response of perchlorate anions (Figure 2(vi)) using Eq. (2). For the voltammetric responses of the other anion transfer reactions (Figure 2(ii-v)), we estimated the half-wave transfer potential for each anion by measuring the potential of each anion required to obtain the same current value as the $I_{1/2, \text{ClO}_4^-}$ value. Next, the formal transfer potential of each anion was determined from the corresponding experimental half-wave potential using the modified equation of inlaid micro-disc interface expressed by:¹⁰

$$\Delta_o^w \phi_{1/2, A^-} = \Delta_o^w \phi_{A^-}^{\theta'} + \frac{RT}{zF} \ln \left(\frac{D^w \gamma^o}{D^o \gamma^w} \right) + \frac{RT}{zF} \ln \left(\frac{4d}{\pi r} + 1 \right) \quad (3)$$

where, d is the thickness and r is the radius of microhole.

Table 1. Summary of estimated values of the half-wave potential, the formal transfer potential and the formal Gibbs transfer energy for the transfer of various anions across the 66 microhole array-aqueous/PVC-NPOE gel interface

Ion	$\Delta_o^w \phi_{1/2, A^-} / \text{mV}$	$\Delta_o^w \phi_{A^-}^{\theta'} / \text{mV}$	$\Delta_o^w G_{\text{tr}, A^-}^{o', w \rightarrow o} / \text{kJ mol}^{-1}$
ClO_4^-	-290.8 ± 15	-379.8 ± 15	-36.6 ± 1.5
SCN^-	-389.4 ± 15	-478.4 ± 15	-46.2 ± 1.5
I^-	-425.1 ± 15	-514.1 ± 15	-49.6 ± 1.5
NO_3^-	-491.7 ± 15	-580.7 ± 15	-56.0 ± 1.5
Br^-	-523.7 ± 15	-612.7 ± 15	-59.1 ± 1.5

Note: $\Delta_o^w \phi_{1/2, A^-}$ is the half-wave potential of an anionic species (A^-). $\Delta_o^w \phi_{A^-}^{\theta'}$ is the formal transfer potentials of A^- species in the TATB potential scale using TMA^+ ion as an internal reference. $\Delta_o^w G_{\text{tr}, A^-}^{o', w \rightarrow o}$ is the formal Gibbs energy of transfer of anions in the TATB scale across the water/3% PVC-NPOE gel interface. For TMA^+ ion, $\Delta_o^w \phi_{1/2}$, $\Delta_o^w \phi_{\text{TMA}^+}^{\theta'}$ and $\Delta_o^w G_{\text{tr}, \text{TMA}^+}^{o', w \rightarrow o}$ were evaluated as 214.0 ± 15 mV, 125.0 ± 15 mV and 12.1 ± 1.5 , respectively.

The activity coefficients in water (γ^w) and organic gel (γ^o) have been assumed as equal. The ratio of diffusion coefficients between the aqueous and PVC-NPOE gel (D^w/D^o) is considered as 1/13.8 which is equal to the ratio between water and pure NPOE described previously.¹⁰ Using the given information and the estimated half-wave potential of each anion from Figure 2, we were able to evaluate the formal transfer potential of all studied anions across the microhole array-water/3% PVC-NPOE gel using Eq. (3).

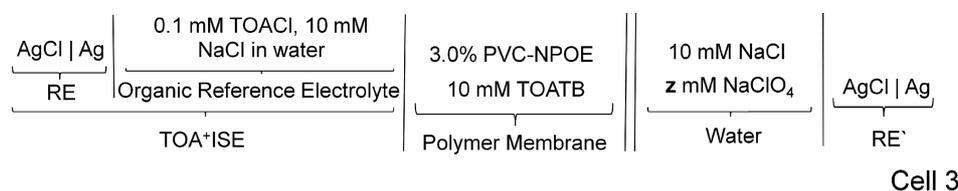
The formal Gibbs transfer energies of various anions were finally calculated using the following equation with the estimated formal transfer potential of each anion:

$$\Delta_o^w G_{\text{tr}, A^-}^{o', w \rightarrow o} = -z_i F \Delta_o^w \phi_{A^-}^{\theta'} \quad (4)$$

where, $\Delta_o^w \phi_{A^-}^{\theta'}$ is the formal transfer potential of anions. The calculated formal Gibbs transfer energies using Eq. (4) alongside the estimated values of half-wave potentials and the calculated formal transfer potentials for Br^- , NO_3^- , I^- , SCN^- and ClO_4^- are summarized in Table 1.

The more negative value of the formal Gibbs transfer energies for anions indicates that a more negative applied potential is required to drive the anion transfer reaction from the aqueous to the organic phase or *vice versa*. Results showing that the negative values of the formal Gibbs transfer energies increased from ClO_4^- to Br^- anions in Table 1 are in good agreement with the lipophilicity sequences of anions in the Hofmeister series.²⁵

Perchlorate Anion Transfer Across a Microhole Array-Water/Gel Interface for Sensing Applications. Perchlorate transfer reactions across the liquid/gel interface as a function of the concentration were studied using cyclic voltammetry and the electrochemical cell set-up, Cell 3.



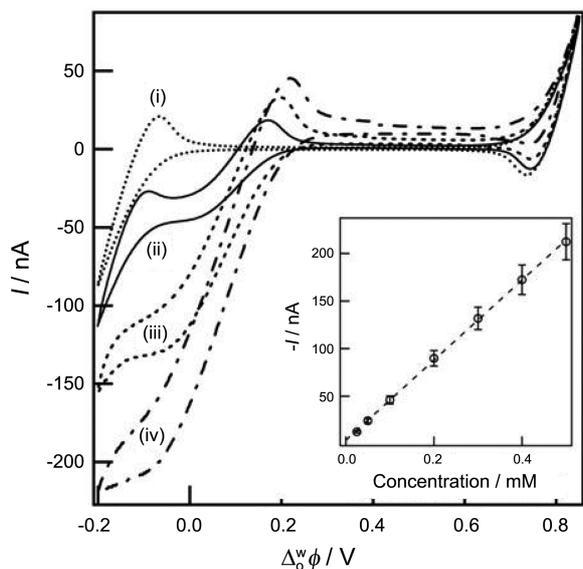


Figure 3. A series of cyclic voltammograms for different concentrations of perchlorate ion transfer across the microhole array interface between water and the PVC-NPOE gel phase using Cell 3. 10 mM NaCl in (i) the absence of perchlorate ion and in the presence of (ii) 0.1 mM (iii) 0.3 mM and (iv) 0.5 mM perchlorate ions. Scan rate = $20 \text{ mV}\cdot\text{s}^{-1}$. Inset shows a plot of the steady-state current versus the perchlorate ion concentration ranging from 0.025 to 0.5 mM. Dotted line shows a linear fit.

Figure 3 represents a series of cyclic voltammograms for the direct transfer reaction of different concentrations of the perchlorate anion across the polarized microhole-liquid/PVC-NPOE gel interface. In the absence of perchlorate (Figure 3(i)), no steady-state current was observed within the given potential window set by Na^+ or TB^- at the positive end potential and TOA^+ or Cl^- at the negative end potential. With the addition of perchlorate anions in the aqueous phase, a steady-state current on the forward scan was observed due to the hemi-spherical diffusion of perchlorate ions from the aqueous to organic phase, while a peak-shaped voltammogram on the reverse scan was observed mainly due to the linear diffusion flux of perchlorate ions transferring from the organic to the aqueous phase. The steady-state current was observed to increase linearly versus the perchlorate anion concentration with a linear slope of $420.67 \text{ nA}\cdot\text{mM}^{-1}$ (see Figure 3 Inset) with a minimum detection limit of about $2 \mu\text{M}$ of perchlorate anions.

The use of differential pulse stripping voltammetry (DPSV) was next investigated with an effort to improve the sensitivity of perchlorate anion sensing in conjunction with a preconcentration step which accumulates perchlorate anions in the organic gel layer by applying a potential of 170 mV for 40 s where the perchlorate transfers from the aqueous to organic gel phase. The accumulated perchlorate ions were then stripped from the organic gel layer to the aqueous phase by sweeping the applied potential from -200 mV to 450 mV with a potential increment of $10 \text{ mV}\cdot\text{s}^{-1}$. Figure 4 represents a series of DPS voltammograms for the various concentrations of perchlorate ions with a peak current corresponding to the perchlorate ion stripped from the organic gel layer to

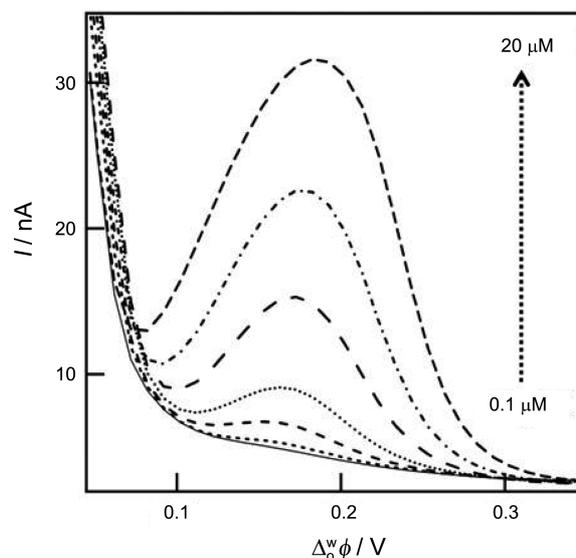


Figure 4. Differential pulse stripping voltammograms obtained for the transfer of perchlorate anions from the organic gel layer to water phase at concentrations of 0.1, 0.5, 2, 5, 10 and $20 \mu\text{M}$ (dotted lines). The scan is directed from a low to high positive potential to drive the perchlorate ion transfer from the PVC-NPOE gel layer to the aqueous phase containing different concentrations of perchlorate anions. The solid line represents the DPSV data obtained in the absence of the perchlorate ion. A deposition potential of 170 mV for 40 s prior to analysis was applied for accumulating perchlorate anions in the gel layer. Potential increment = 10 mV, pulse potential = 50 mV, pulse duration = 50 ms.

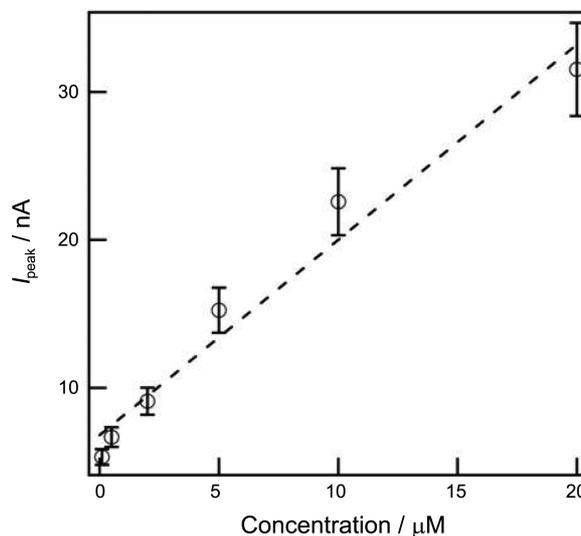


Figure 5. A plot of the peak current value obtained from the DPSV results in Figure 4 as a function of the perchlorate concentration ranging from 0.1 to $20 \mu\text{M}$. Dotted line represents a linear fit.

the aqueous phase. From the plot of the peak current versus the perchlorate concentration in Figure 5, a linear fit with a slope of $1.32 \text{ nA}\cdot\mu\text{M}^{-1}$ for the concentrations varying from $0.1 \mu\text{M}$ to $20 \mu\text{M}$ was achieved. A superb detection limit of $0.1 \mu\text{M}$ using a signal to noise ratio of 3:1 was obtained which can be employed to a perchlorate analysis. In order to demonstrate real field applicability, the recovery test for the different sets of perchlorate samples was performed; a

Table 2. Amperometric selectivity coefficients of the perchlorate sensing signal over different interfering anions

Interfering anion	SCN ⁻	I ⁻	NO ₃ ⁻	Br ⁻	Cl ⁻	NO ₂ ⁻	HCO ₃ ⁻	CH ₃ COO ⁻	SO ₄ ²⁻
log $k_{i,j}^{\text{amp}}$	-1.32	-2.58	-3.69	-3.71	<i>n.i.</i>	<i>n.i.</i>	<i>n.i.</i>	<i>n.i.</i>	<i>n.i.</i>

n.i.: not interfering.

satisfactory recovery of perchlorate ions with $\pm 7\%$ variation was obtained, which can be considered as an acceptable error range for on-site sensing applications.

As a final demonstration, the selectivity of the amperometric perchlorate sensing platform over various interfering anionic species was studied using the fixed analyte concentration method,²⁶ utilizing Eq. (5) and a fixed concentration of 10 μM perchlorate:

$$k_{i,j}^{\text{amp}} = (I_i - I_j)C_i / I_i C_j \quad (5)$$

where, i and j are the analyte and the interfering agent, respectively and I_i is the total current from both the analyte and interfering agent. The selectivity of perchlorate sensors is mainly dependent on the thermodynamic properties of the interfering ions. The thermodynamic values presented in Table 1 show that some anions (*i.e.*, SCN⁻, I⁻) have similar values for the formal transfer potential and the formal Gibbs transfer energy compared to that of the perchlorate anion. It can thus be assumed that these anions will interfere at a significant level with the perchlorate sensing signal. On the other hand, a very small or negligible interference is expected for anions (NO₃⁻, Br⁻ and Cl⁻) which have much higher negative values of the formal transfer potentials and higher formal Gibbs transfer energies than that of the perchlorate anion. The amperometric selectivity coefficient obtained for the microhole array perchlorate sensing platform over different interfering anions including SCN⁻, I⁻, NO₃⁻, Br⁻, Cl⁻, NO₂⁻, HCO₃⁻, CH₃COO⁻ and SO₄²⁻ is presented in Table 2. The sensing signal for perchlorate anion showed a negligible interference up to a 100 fold excess of each interfering anions including nitrate, bromide, chloride, nitrite, bicarbonate, acetate, and sulfate. This is probably due to the fact that those anions possess much higher values of the formal Gibbs energy of transfer than that of the perchlorate anion which results in requiring the more negative potential for the interfering anions to transfer across the interface. Note that some anions such as thiocyanate and iodide which have a similar value of the formal Gibbs transfer energy to that of perchlorate anions exhibit significant interferences on the perchlorate sensing signals which will be further investigated in the future.

Conclusions

The transfer behavior of very hydrophilic anions across a 66 microhole array interface between an aqueous and a PVC-NPOE gel phase incorporating TOATB organic supporting electrolyte was characterized. The newly synthesized TOATB salt shows an excellent electrochemical behavior as an organic supporting electrolyte providing a wide

potential window at the negative end potential for assisting the transfer of various hydrophilic anions at the micro-water/gel interface. Thermodynamic information including the half-wave potentials, the formal transfer potentials and the formal Gibbs transfer energies for the transfer of hydrophilic anionic species including Br⁻, NO₃⁻, I⁻, SCN⁻ and ClO₄⁻ were also evaluated. As a demonstration, the direct transfer reaction of perchlorate ions across the micro-liquid/gel interface was investigated for the anion sensitive sensing applicability of the microhole-liquid/gel interface; a detection limit of 0.1 μM with a wide linearity ranging from 0.1 to 20 μM was achieved. We envision that the amperometric anion sensing approach utilizing the liquid/gel interface with a hydrophobic organic supporting electrolyte can be implemented for the sensitive detection of a wide spectrum of hazardous anionic substances in water samples.

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