J Solid State Electrochem (2009) 13:1475–1482
DOI 10.1007/s10008-008-0709-x

ORIGINAL PAPER

Boronic acid-facilitated α-hydroxy-carboxylate anion transfer at liquid/liquid electrode systems: the EIC_{rev} mechanism

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Received: 14 August 2008 / Revised: 19 September 2008 / Accepted: 10 October 2008 / Published online: 31 October 2008

Abstract The transfer of the α-hydroxy-carboxylates of glycolic, lactic, mandelic and gluconic acid from the aqueous electrolyte phase into an organic 4-(3-phenyl-propyl)-pyridine (PPP) phase is studied at a triple-phase boundary electrode system. The tetraphenylporphyrinato complex MnTPP dissolved in PPP is employed to drive the anion transfer reaction and naphthalene-2-boronic acid (NBA) is employed as a facilitator. In the absence of a facilitator, the ability of α-hydroxy-carboxylates to transfer into the organic phase improves, consistent with hydrophobicity considerations giving relative transfer potentials (for aqueous 0.1 M solution) of gluconate>glycolate>lactate> mandelate. In the presence of NBA, a shift of the reversible transfer potential to more negative values is indicating fast reversible binding (the mechanism for the electrode process is EIC_{rev}) and the binding constants are determined as $K_{glycolate}$=2 M^{-1}, $K_{mandelate}$=60 M^{-1}, $K_{lactate}$=130 M^{-1} and $K_{gluconate}$=2,000 M^{-1}. The surprisingly strong interaction for gluconate is rationalised based on secondary interactions between the gluconate anion and NBA.

Keywords Boronic acid · Carbohydrate · α-Hydroxy carboxylic acid · Voltammetry · Liquid/liquid interface · Electrocatalysis · Sensors

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Introduction

Electrochemical processes occur at polarised interfaces where the applied potential causes interfacial electron transfer. Reversibly coupled to this electron transfer step, further processes such as chemical reactions [1] or interfacial ion transfer reactions [2] may occur. For both of these types of processes, the shift in the measured potential versus a reference potential reveals the magnitude of the associated equilibrium constant (chemical or interfacial). Data for ion transfer equilibria between two immiscible liquid phases are directly accessible with four-probe potentiostatic measurements [3, 4] where both liquid phases contain supporting electrolyte to aid conduction. Alternatively, micro-droplets of the organic liquid phase without intentionally added supporting electrolyte [5, 6] but with a suitable redox system deposited onto the working electrode in a three-probe potentiostated measurement cell have been employed for the study of ion transfer equilibria [7]. The present study utilises the micro-droplet approach for the study of facilitated anion transfer in the presence of naphthalene-2-boronic acid (NBA).

Facilitated ion transfer is a well-known process [8] with applications in metal ion extraction [9], selective ion detection [10] and for processes in porous solids [11]. Chelators are often employed to facilitate the transfer of specific metal cations [12]. In this study, a boronic acid facilitator is introduced to enhance the transfer of α-hydroxy-carboxylates. Boronic acids are well-known for their interaction with diols [13], carbohydrates [14, 15], hydroxy-carboxylates [16–18] and some amino acids [19]. Boronic acid molecular receptors have been designed to bind to drugs and to facilitate the drug transfer across lipid membranes in cell walls [20]. In this study, the ability of a highly lipophilic boronic acid derivative, NBA, to facilitate

the transfer of α-hydroxy-carboxylates from an aqueous into an organic phase is quantified based on micro-droplet voltammetry.

Micro-droplets of water-immiscible organic liquids are readily formed on suitable electrode surfaces [21] and redox systems have been proposed to study the transfer of cations [22], of anions [23] or both [24] from the aqueous into the organic phase. The transfer of carboxylate anions was studied for nitrobenzene [25] and for 4-(3-phenylpropyl)-pyridine (PPP) [26] liquids.

Figure 1 shows a schematic diagram indicating the simple ion transfer case (the EI mechanism [27]; see Fig. 1a) where the oxidation of a Mn(II) redox system within the organic phase is coupled to the transfer of the anion A^-. In the presence of a boronic acid facilitator, an additional fast equilibration process occurs within the organic phase (the EIC_{rev} mechanism; see Fig. 1b) and a complex AB^- is formed.

This study demonstrates that fast equilibration processes in micro-droplet environments are conveniently measured in three-electrode voltammetric experiments. Quantitative binding constant are obtained and this will allow a wider range of boronic acid derivatives to be studied and optimised, for example, for targeted anion extraction.

Experimental details

Chemical reagents

L(+)-lactic acid solution 85–90 wt.%, glycolic acid, mandelic acid, D-gluconic acid solution 45–50 wt.%, NaOH, PPP, $NaClO_4$ and 5,10,15,20-tetraphenyl-21H,23H-porphine manganese(III) chloride were obtained from Aldrich and used without additional purification. Naphtalene-2-boronic acid was obtained from Frontier Scientific. De-mineralised and filtered water was taken from a Vivendi water purification system with not less than 18 MΩ cm resistivity.

Instrumentation

Voltammetric experiments were performed with a micro-Autolab III system (Ecochemie, the Netherlands) in staircase voltammetry mode. The step potential was maintained at approximately 1 mV. The counter and reference electrode were platinum gauze and saturated calomel (SCE, Radiometer), respectively. The working electrode was a 4.9-mm diameter basal plane pyrolytic graphite disc (BPPG, Pyrocarbon, Le Carbon, UK) mounted in Teflon. Solutions were de-aerated with argon (Pureshield, BOC). The pH of the solutions of lactic, glycolic, mandelic or gluconic acid was adjusted to approximately 7 by addition of sodium hydroxide. The pH was measured with a glass electrode (3505 pH meter, Jenway). All experiments were conducted at a temperature of 22±2 °C.

Formation of micro-droplet deposits

A solution of tetraphenylporphyrinato-manganese(III) chloride (MnTPPCl) and PPP in acetonitrile was prepared with typically 4 mg MnTPPCl and 80 mg PPP in 10 mL of acetonitrile. A volume of typically 10 μL of this solution was then transferred onto the BPPG surface. Following acetonitrile evaporation, a micro-droplet deposit of approximately 75 nL PPP containing approximately 75 mM MnTPPCl was obtained. Co-evaporation of solutions containing NBA in acetonitrile was employed to introduce the boronic acid.

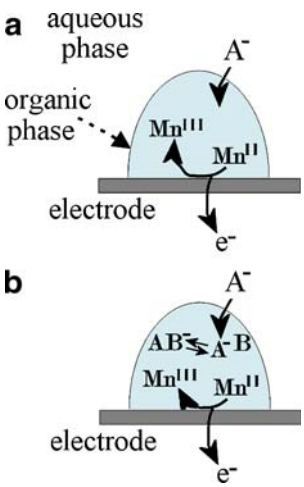


Fig. 1 Schematic representation of processes in a micro-droplet of organic liquid deposited onto an electrode and immersed in aqueous solution: **a** coupled electron and anion transfer for the EI process and **b** coupled electron and anion transfer followed by a fast chemical equilibrium process for the EIC_{rev} process

Theory

The transfer of an anion from the aqueous into the organic micro-droplet phase occurs upon one electron oxidation of the redox system immobilised within the organic phase (see Eq. 1):

$$\mathrm{Red(oil)} + \mathrm{A^-(aq)} \rightleftarrows \mathrm{Ox^+(oil)} + \mathrm{A^-(oil)} + \mathrm{e^-}. \qquad (1)$$

In this equation, Red and Ox^+ denote the Mn(II)TPP and $Mn(III)TPP^+$ metal complexes and A^- stands for the transferring anion. The appropriate Nernst equation (without taking into account activity effects) associated with this process is given in Eq. 2. Based on this and under

conditions where $[Ox^+(oil)]=[Red(oil)=\frac{c_0}{2}]$ Eq. 3 can be obtained:

$$E_{rev} = E^{0\prime} + \frac{RT}{F}\ln\left(\frac{[Ox^+(oil)][A^-(oil)]}{[Red(oil)][A^-(aq)]}\right), \quad (2)$$

$$E_{rev1/2} = E^{0\prime} + \frac{RT}{F}\ln\left(\frac{c_0}{2}\right) - \frac{RT}{F}\ln([A^-(aq)]). \quad (3)$$

It has been proposed [28] that the midpoint potential E_{mid} (obtained from experimental voltammograms as the midpoint between anodic and cathodic peak potential) can be expressed approximately as $E_{rev1/2} \approx E_{mid}$ (although the agreement of this expression with experimental data can be limited to the second term $\frac{RT}{F}\ln([A^-(aq)])$ [27]).

It is possible to introduce a fast equilibrium in which the anion $A^-(oil)$ is forming a complex with B (denoting boronic acid, see Eqs. 4 and 5) with a binding constant K_{AB}:

$$A^-(oil) + B(oil) \rightleftarrows AB^-(oil), \quad (4)$$

$$K_{AB} = \frac{[AB^-(oil)]}{[A^-(oil)][B(oil)]}. \quad (5)$$

Under these conditions, the total concentrations of $A^-(oil)$ and of B(oil) are given by the sum of the bound and unbound species (Eqs. 6 and 7):

$$[A_t^-(oil)] = [A^-(oil)] + [AB^-(oil)], \quad (6)$$

$$[B_t(oil)] = [B(oil)] + [AB^-(oil)], \quad (7)$$

Equations 5, 6 and 7 can be solved simultaneously (by inserting Eqs. 6 and 7 into Eq. 5 and solving the resulting quadratic equation) in order to express $[A^-(oil)]$ (see Eq. 8):

$$[A^-(oil)] = [A_t^-(oil)] \times \frac{1}{[A_t^-(oil)]}\left(-\frac{X}{2} + \sqrt{\frac{X^2}{4} + \frac{[A_t^-(oil)]}{K_{AB}}}\right).$$
$$\text{with} \quad X = 1/K_{AB} - [A_t^-(oil)] + [B_t(oil)] \quad (8)$$

Finally, the reversible potential for $[Ox^+(oil)]=[Red(oil)]$ (compare Eqs. 2 and 3) is now given by Eq. 9:

$$E_{rev1/2} = E^{0\prime} + \frac{RT}{F}\ln\left(\frac{c_0}{2}\right) - \frac{RT}{F}\ln([A^-(aq)]) + \Delta E$$
$$\text{with} \quad \Delta E = \frac{RT}{F}\ln\left(\frac{1}{[A_t^-(oil)]}\left(-\frac{X}{2} + \sqrt{\frac{X^2}{4} + \frac{[A_t^-(oil)]}{K_{AB}}}\right)\right). \quad (9)$$

The shift in the midpoint potential E_{mid} obtained from experimental voltammograms can, therefore, be expressed as ΔE and calculated based only on known concentration data and the binding constant K_{AB}. Binding constants are evaluated by matching experimental E_{mid} data and expression 9 in an Excel spreadsheet.

Results and discussion

The effect of boronic acid on the transfer of perchlorate anions across the 4-(3-phenylpropyl)-pyridine/aqueous electrolyte interface

The metal complex MnTPP (introduced in the form of the chloride Mn(III)TPPCl) dissolved into the water-immiscible solvent PPP is employed as redox system. For this system, the facile transfer of anions from the aqueous into the organic phase has been demonstrated previously for anions such as PF_6^-, ClO_4^- and NO_3^- [29] and for carboxylates [26]. In this study, the effect of NBA (added into the organic PPP phase) on the transfer of perchlorate from the aqueous into the organic phase is studied in order to provide a baseline check for anion transfer processes without significant interaction with boronic acid. Experiments were conducted by immersion of the Mn(III)TPPCl containing micro-droplets into the aqueous electrolyte. However, the chloride anion was expected to exchange rapidly without affecting the experimental data. In order to minimise potential interference from chloride, all voltammetric experiments were initiated after equilibration at a negative potential where the reduced form Mn(II)TPP is present and, therefore, without counter anion.

Figure 2 shows a set of cyclic voltammograms obtained without and with the presence of NBA. A well-defined voltammetric response is observed with a reversible midpoint potential (calculated from $E_{mid} = \frac{E_p^{ox}+E_p^{red}}{2}$) for the Mn(III/II) system at −0.273 V versus SCE (see Fig. 2b).

The amount of NBA added in this experiment is substantial. The highest level (see data point (vii) in Fig. 2b) corresponds to a molar ratio of approximately 1:1 PPP to NBA. This high content may affect the volume and viscosity of the micro-droplet deposit, which explains the

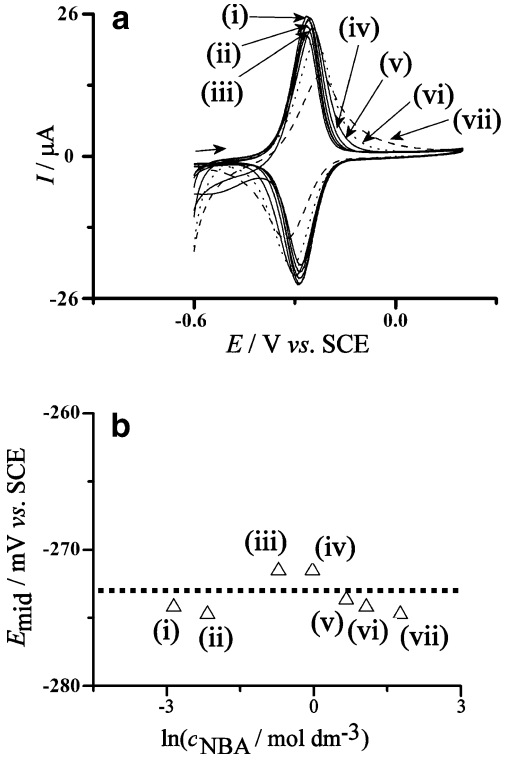


Fig. 2 **a** Cyclic voltammograms (scan rate 10 mV s^{-1}) for the oxidation and re-reduction of MnTPP (75 mM) in PPP (75 nL) deposited from acetonitrile onto a 4.9-mm diameter BPPG electrode and immersed in aqueous 0.1 M $NaClO_4$. The concentration of NBA was varied as indicated. **b** Plot of the midpoint potential E_{mid} for perchlorate transfer versus the natural logarithm of the concentration of NBA

slight decrease in peak current and the increase in peak-to-peak separation (see Fig. 2a). However, the midpoint potential for the perchlorate anion transfer is not affected by the presence of boronic acid. The overall process for the perchlorate anion transfer can be expressed in a two-step mechanism consistent with an EI process [27] (Eqs. 10 and 11):

$$\mathrm{E-step:}\quad \mathrm{MnTPP(II)(org)} \rightleftarrows \mathrm{MnTPP(II)^{+}(org)} + \mathrm{e^{-}}, \tag{10}$$

$$\mathrm{I-step:}\quad \mathrm{ClO_4^{-}(aq)} \rightleftarrows \mathrm{ClO_4^{-}(org)}. \tag{11}$$

The effect of boronic acids on the transfer of α-hydroxy-carboxylates across the 4-(3-phenylpropyl)-pyridine/aqueous electrolyte interface I: glycolate

In order to investigate the transfer of α-hydroxy-carboxylates from the aqueous into the organic PPP phase, experiments for the glycolate anion are conducted. A solution 0.1 M in glycolate and adjusted to pH 7.24 is employed. The oxidation and re-reduction of MnTPP are observed as well-defined voltammetric responses with a midpoint potential of +46 mV versus SCE (see Fig. 3a). The effect of the scan rate is investigated and the plot in Fig. 3b clearly shows a linear relationship consistent with a surface immobilised MnTPP in PPP redox system and fast transfer of glycolate.

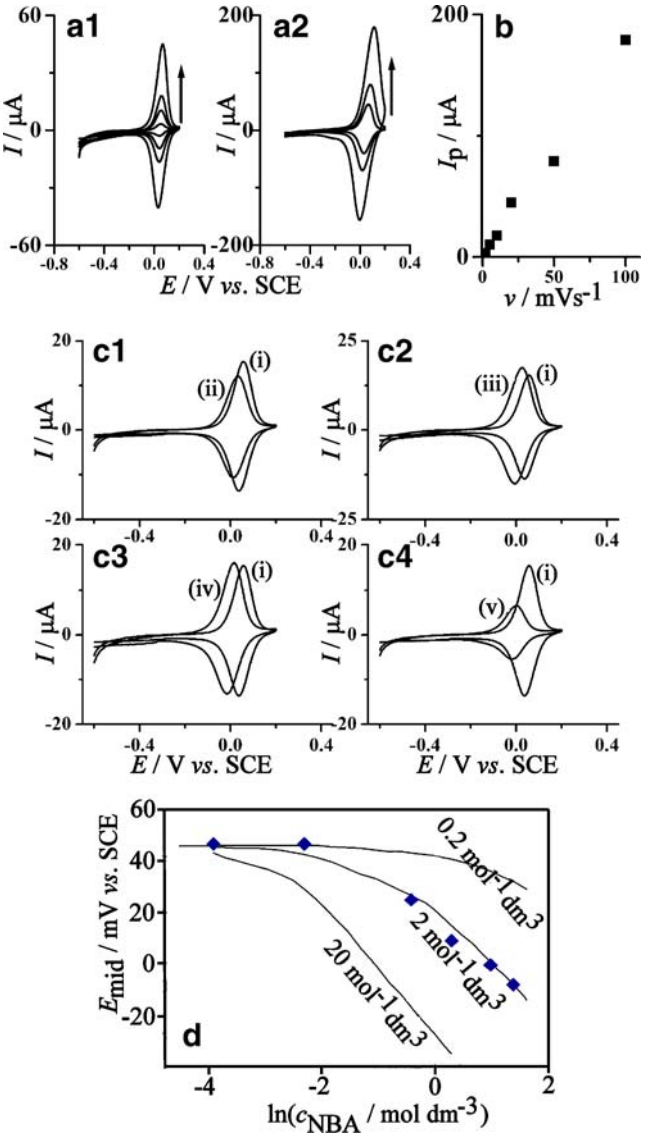


Fig. 3 **a** Cyclic voltammograms (scan rates 2, 5, 10, 20, 50 and 100 mV s^{-1}) for the oxidation and re-reduction of 75 mM MnTPP dissolved in 75 nL PPP and immobilised onto a 4.9-mm diameter BPPG electrode immersed in aqueous 0.1 M sodium glycolate pH 7.24. **b** Plot of the anodic peak current versus scan rate. **c** Cyclic voltammograms (scan rate 10 mV s^{-1}) in the presence of naphthalene-2-bornonic acid (*i*) 0 M, (*ii*) 0.69 M, (*iii*) 1.38 M, (*iv*) 2.76 M and (*v*) 4.14 M concentration. **d** Plot of the midpoint potential for the MnTPP redox system during glycolate transfer versus the natural logarithm of NBA concentration. *Lines* are calculated based on Eq. 9

In the presence of NBA, a clear negative shift of the reversible glycolate transfer response is observed. Figure 3c demonstrates the effect for (i) 0 M, (ii) 0.69 M, (iii) 1.38 M, (iv) 2.76 M and (v) 4.14 M NBA. A plot of the midpoint potential versus the natural logarithm of the NBA concentration is shown in Fig. 3d together with the theoretically predicted trends (see lines) based on Eq. 9 for the EIC_{rev} mechanism (see Eqs. 12, 13 and 14). The binding constant for the interaction of NBA with glycolate in PPP solvent is determined as $K_{glycolate}=2\ mol^{-1}\ dm^3$.

$$E-step: \quad MnTPP(II)(org) \rightleftarrows MnTPP(II)^{+}(org) + e^{-}, \tag{12}$$

$$I-step: \quad Glycolate^{-}(aq) \rightleftarrows Glycolate^{-}(org), \tag{13}$$

$$C_{rev}-step: \quad Glycolate^{-}(org) + NBA(org) \rightleftarrows \{NBA-Glycolate\}^{-}(org). \tag{14}$$

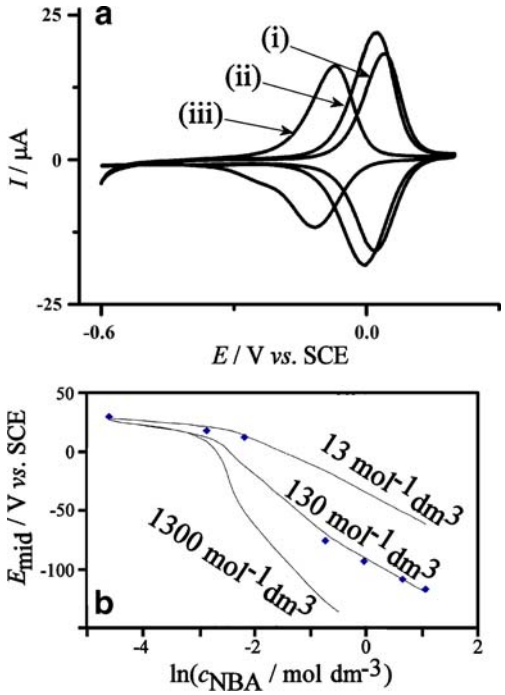


Fig. 4 **a** Cyclic voltammograms (scan rate 10 mV s^{-1}) for the oxidation and re-reduction of 75 mM MnTPP dissolved in PPP (75 nL) and immobilised onto a 4.9-mm diameter BPPG electrode immersed in aqueous 0.1 M sodium lactate pH 7.34. The presence of (*i*) 0 mM, (*ii*) 114 mM and (*iii*) 973 mM NBA is shown to cause a shift in the voltammetric response. **b** Plot of the midpoint potential versus the natural logarithm of the NBA concentration. *Lines* are calculated based on Eq. 9

The effect of boronic acids on the transfer of α-hydroxy-carboxylates across the 4-(3-phenylpropyl)-pyridine/aqueous electrolyte interface II: lactate

Next, experiments are carried out for the transfer of lactate anions. Lactate has an additional methyl substituent and should, therefore, be slightly more hydrophobic. The voltammetric response for the MnTPP oxidation-driven transfer of lactate exhibits a midpoint potential of +30 mV versus SCE which is 16 mV more negative (more hydrophobic) compared to the value for glycolate (see Fig. 4a). Experiments were conducted at a range of pH values from 7 to 12 and no significant effect of the pH was observed consistent with the pK_A 3.08 for lactate [30] and the transfer of the anionic form.

In the presence of NBA, again a systematic shift of the reversible voltammetric response is observed consistent with a facilitated anion transfer. The plot in Fig. 4b demonstrates that the shift in midpoint potential is consistent with a binding constant of $K_{lactate}=130\ mol^{-1}\ dm^3$. It is interesting to note that the effect of boronic acid is "switched on" always in the same concentration range close to the concentration of the MnTPP redox system. Concentrations significantly lower than this are obviously not effective in changing the voltammetric response. In order to work in a lower concentration range, the MnTPP content in the micro-droplet deposit needs to be lowered.

The effect of boronic acids on the transfer of α-hydroxy-carboxylates across the 4-(3-phenylpropyl)-pyridine/aqueous electrolyte interface III: mandelate

Mandelate is investigated as a substantially more hydrophobic anion (due to the phenyl group) and the midpoint potential for the MnTPP oxidation-driven transfer of the mandelate anion is indeed shifted more negative to −90 mV versus SCE (see Fig. 5a). From the shift in the midpoint potential in the presence of NBA (see Fig. 5b), the binding constant $K_{mandelate}=60\ mol^{-1}\ dm^3$ is determined. This value is very similar to that observed for lactate and, therefore, indicating that the anion hydrophobicity is not contributing to the ability to bind to the boronic acid.

The effect of boronic acids on the transfer of α-hydroxy-carboxylates across the 4-(3-phenylpropyl)-pyridine/aqueous electrolyte interface IV: gluconate

Finally, gluconic acid (2,3,4,5,6-pentahydroxycaproic acid) is investigated and the transfer of gluconate from the aqueous phase into the organic PPP phase is monitored. In solution, gluconic acid exhibits three isomeric forms: the

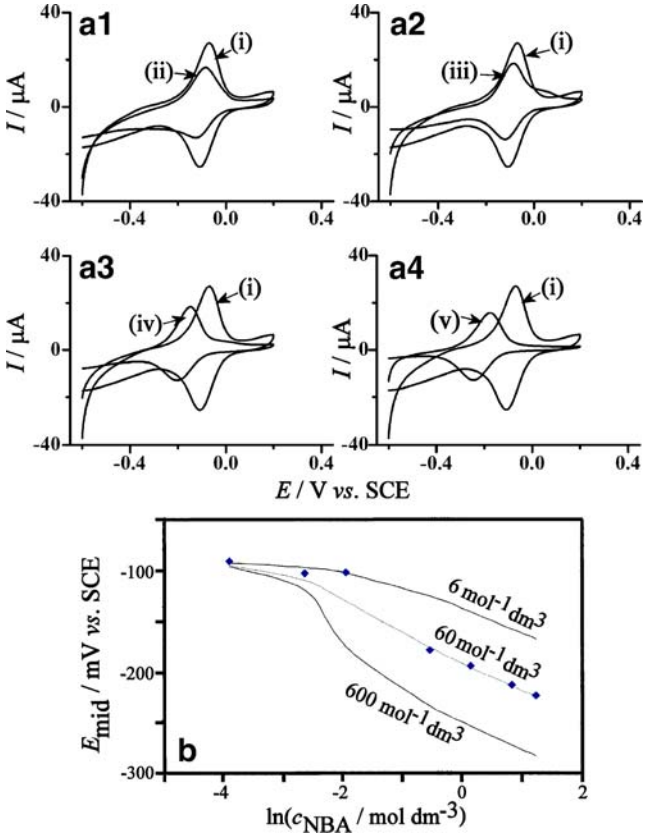


Fig. 5 **a** Cyclic voltammograms (scan rate 10 mV s^{-1}) for the oxidation and re-reduction of 75 mM MnTPP dissolved in 75 nL PPP immobilised onto a 4.9-mm diameter BPPG electrode immersed in aqueous 0.1 sodium mandelate pH 7.27. Voltammograms were obtained in the presence of (*i*) 0 mM, (*ii*) 75 mM, (*iii*) 150 mM, (*iv*) 650 mM and (*v*) 2.5 M NBA. **b** Plot of the midpoint potential versus the natural logarithm of the concentration of NBA. *Lines* are calculated based on Eq. 9

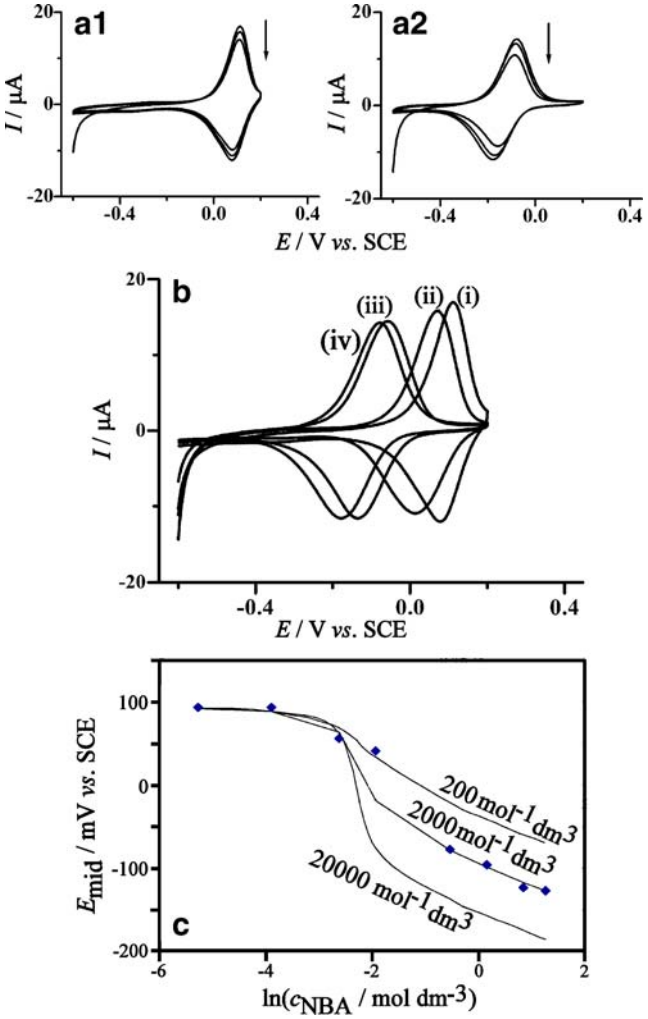


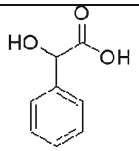
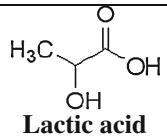
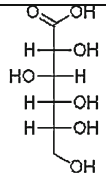
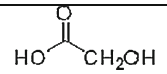
Fig. 6 **a** Cyclic voltammograms (scan rate 10 mV s^{-1}; first, second and fifth potential cycle shown) for the oxidation and re-reduction of 75 mM MnTPP dissolved in 75 nL PPP immobilised onto a 4.9-mm diameter BPPG electrode immersed in aqueous 0.1 M sodium gluconate pH 7.27. Voltammograms were obtained in the presence of 0 and 3.9 M NBA. **b** Cyclic voltammograms (scan rate 10 mV s^{-1}) obtained in the presence of (*i*) 0 M, (*ii*) 0.15 M, (*iii*) 1.3 M and (*iv*) 3.9 M NBA. **c** Plot of the midpoint potential versus the natural logarithm of the concentration of NBA. *Lines* are calculated based on Eq. 9

open anionic or protonated form (at pH>2.5), the δ-lactone (2.5>pH>2) and the γ-lactone (at pH<2) [31]. When supplied commercially, the lactone form is dominant and solution freshly made and adjusted to pH 7.27 exhibited more complex voltammetric behaviour (not shown). The midpoint potential for the voltammetric response was observed to shift and stabilise over a period of 3–4 h, which is consistent with the equilibration process involving lactone ring-opening in the aqueous solution. Pre-equilibrated solutions (left 24 h at room temperature) give simple voltammetric responses and are used for the experiments described below.

Figure 6a shows typical cyclic voltammograms for the MnTPP oxidation-driven transfer of gluconate anions from the aqueous into the organic PPP phase. The gluconate transfer from 0.1 M aqueous solution occurs at a midpoint potential of +94 mV versus SCE which is indicative of the highly hydrophilic nature of this anion. The presence of several hydroxyl groups allow good interaction with water molecules and make transfer into the organic phase more energetically unfavourable.

The presence of NBA causes a significant shift in the midpoint potential for the gluconate transfer (see Fig. 6b) and the binding constant in this case is evaluated as $K_{\text{gluconate}}$=2,000 mol^{-1} dm^3 (see Fig. 6c). This binding constant is substantially higher when compared to those for glycolate, lactate and mandelate probably due to additional interactions of the hydroxyl functionalities in gluconate with the NBA facilitator (see Table 1).

Table 1 Summary of the chemical structures of α-hydroxy carboxylic acids, physical constants and measured transfer potentials and equilibrium constants

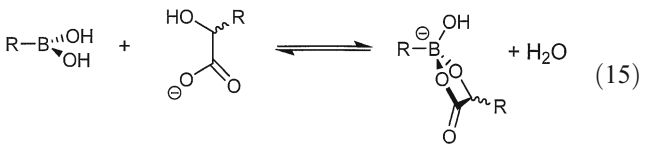
Structures	Transfer potential E_{mid} / mV vs. SCE [b]	Binding equilibrium constant K / mol^{-1} dm^3 [c]	pK_A [30]
 Mandelic acid	-90	60	3.85
 Lactic acid	30	130	3.08
 Gluconic acid	94	2000	3.60
 Glycolic acid	46	2	3.83

All measurements were carried out at 20±2 °C

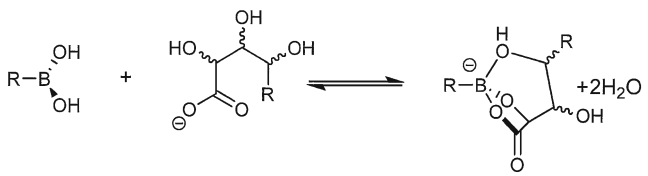
[a] E_{mid} was obtained from cyclic voltammograms based on $E_{mid} = \frac{E_p^{ox} + E_p^{red}}{2}$

[b] Obtained by fitting Eq. 9 to the experimental data. Estimated error ±10%

The proposed structural details for the binding of boronic acid to glycolate, lactate and mandelate (see Eq. 15) and to gluconate (see Eq. 16) are given below:



(15)



(16)

The use of boronic acid derivatives for facilitating the transfer of complex anions (e.g. those with biological relevance including many carboxylates and amino acids) is possible but requires a sufficiently hydrophobic boronic acid system. In the future, the boronic acid facilitator could be further tailored to improve binding, chemoselectivity and enantioselectivity.

Conclusions

It has been shown that α-hydroxy-carboxylates are readily transferred from the aqueous into the organic PPP phase and that boronic acids facilitate this transfer. Both transfer potentials and binding constants were determined and rationalised. This work opens up new opportunities (1) for the more systematic study of the transfer of various biologically or medically important species (e.g. to mimic transport across biological cell walls) and (2) for the design and optimisation of new "facilitators" with higher selectivity. In the future, the concept of the boronic acid facilitator may also be applied for the case of chiral molecules [32] or neutral molecules such as glucose due to the possible formation of an anionic species upon glucose–boronic acid binding in the organic phase [15].

Acknowledgement NK thanks the RSC and EPSRC for the award of an Analytical Studentship. JSF thanks the Leverhulme Trust (F/00/351/P) and the Royal Society Research Grants Scheme (2007/R2). Financial support for AMK from the Leverhulme Trust (F/00351/R) is gratefully acknowledged.

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