

Cite this: *Chem. Commun.*, 2011, **47**, 12002–12004

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## Liquid|liquid electrochemical bicarbonate and carbonate capture facilitated by boronic acids

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Received 22nd August 2011, Accepted 12th September 2011

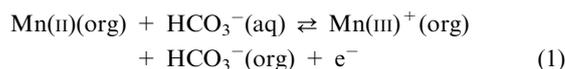
DOI: 10.1039/c1cc15211d

**Reversible bicarbonate and carbonate liquid|liquid ion transfer processes from aqueous solution into an organic 4-(3-phenylpropyl)pyridine phase are driven electrochemically with TPPMn(III/II) and shown to be facilitated over a wide pH range by 2-naphthylboronic acid (bicarbonate transfer potential  $-0.08$  V vs. SCE; binding constant  $K_{AB} = 10^2 \text{ mol}^{-1} \text{ dm}^3$  and carbonate dianion transfer potential  $0.07$  V vs. SCE; binding constant  $K_{AB2} = 2 \times 10^{10} \text{ mol}^{-2} \text{ dm}^6$ ).**

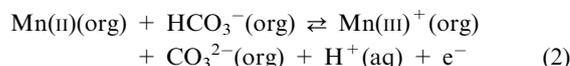
Electrochemical ion transfer at liquid|liquid interfaces is an important and abundant process<sup>1</sup> with applications in sensing<sup>2</sup> and in drug screening and development.<sup>3</sup> It has recently been shown that facilitated ion transfer—that is, ion transfer coupled to additional complexation in the organic phase—can be readily studied when using cyclic voltammetry and droplet deposits of organic oils on appropriate electrode surfaces.<sup>4,5</sup> Many types of facilitated cation and anion transfer (facilitator = ionophore) are known.<sup>6</sup> For anions such as  $\alpha$ -hydroxycarboxylates or  $\alpha$ -amino-carboxylates a facilitator system can be based on boronic acids.<sup>7</sup> Boronic acids have been employed for selective complexation of a wider range of biologically relevant anions<sup>8</sup> including diols and sugars<sup>9</sup> and are proposed here for carbonate dianion complexation. Carbonate complexation by urea derivatives was proposed by Gale and coworkers.<sup>10</sup> Here, transfer and boronic acid binding to bicarbonate and carbonate in a oil|aqueous liquid|liquid system is investigated quantitatively.

A versatile redox system for anion transfer experiments<sup>†</sup> in microdroplets of 4-(3-phenylpropyl)pyridine (PPP) is tetraphenylporphyrinato-Mn(III/II) or TPPMn(III/II). In previous studies this redox system was deposited in the form of microdroplets onto a graphite working electrode for the transfer of perchlorate, nitrate, thiocyanate,<sup>11</sup> as well as for mono-, di-, and tri-carboxylates.<sup>12</sup> Fig. 1A shows a schematic representation of the microdroplet-based process. Oxidation of the tetraphenylporphyrinato Mn(II) to Mn(III)<sup>+</sup> causes re-equilibration of charges associated with transfer of anion A<sup>−</sup> from the aqueous into the organic phase. Immersed into an aqueous solution of 0.1 M NaHCO<sub>3</sub>, a graphite working electrode with 90 mM TPPMn(II) immobilised in PPP solvent allows chemically

reversible voltammetric responses to be obtained (Fig. 1Bv) centered at  $E_{\text{mid}} = 1/2 (E_p^{\text{ox}} + E_p^{\text{red}}) = -0.08$  V vs. SCE. The process is consistent with a bicarbonate transfer (eqn (1)).

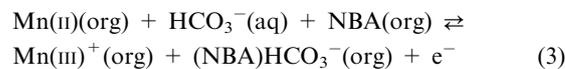


A second process occurs at  $E_{\text{mid}} = 0.07$  V vs. SCE consistent with the transfer of a proton from the oil phase back into the aqueous phase (eqn (2)).



The net process of eqn (1) and (2) together corresponds to carbonate dianion transfer. The energetically unfavorable second process competes successfully in the case of sufficiently extended droplet sizes, at higher scan rates, and in more alkaline solutions (Fig. 1Bi). Effects from direct coordination of carbonate to TPPMn(III)<sup>+</sup>(org) in particular at higher concentrations cannot be entirely ruled out, but have been insignificant in previous studies.<sup>12</sup>

When 2-naphthylboronic acid (NBA) is added into the organic phase a characteristic shift of the  $E_{\text{mid}}$  potential of the voltammetric signal occurs systematically to more negative potentials with increasing boronic acid concentration (Fig. 1Bii–iv). The shift suggests complexation of bicarbonate by boronic acid (eqn (3)) with a corresponding expression for the  $\Delta E_{\text{mid}}$  shift (eqn (4)).<sup>7</sup>



$$E_{\text{rev}1/2} = E^0 + \frac{RT}{F} \ln\left(\frac{c_0}{2}\right) - \frac{RT}{F} \ln([A^-(\text{aq})]) + \Delta E_{\text{mid}} \quad (4)$$

with

$$\Delta E_{\text{mid}} = \frac{RT}{F} \ln\left(\frac{1}{[A_i^-(\text{oil})]} \left(-\frac{X}{2} + \sqrt{\frac{X^2}{4} + \frac{[A_i^-(\text{oil})]}{K_{AB}}}\right)\right)$$

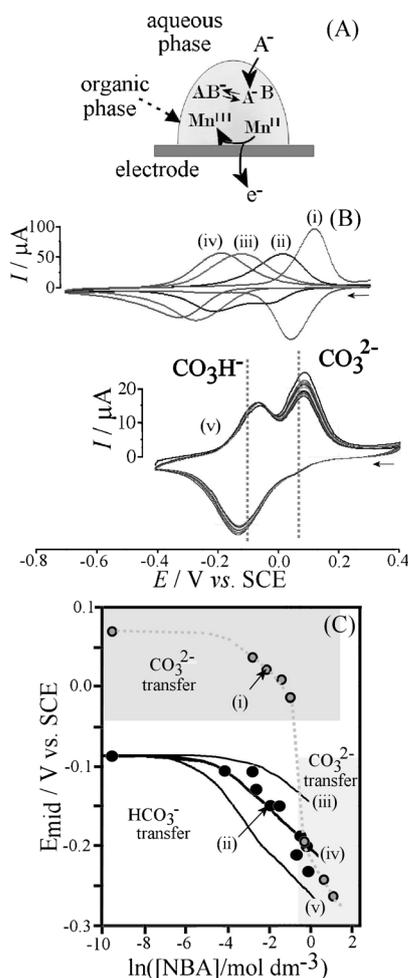
$$X = 1/K_{AB} - [A^-(\text{oil})] + [B_i(\text{oil})]$$

$$K_{AB} = \frac{[AB^-(\text{oil})]}{[A^-(\text{oil})] \times [B(\text{oil})]}$$

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Here  $[A^-_{i(oil)}]$  and  $[B_i(oil)]$  are the known total concentrations of anion and boronic acid in the oil phase,  $c_0$  is the initial concentration of TPPMn,  $E^0$  here is the formal potential for the organic redox system including the potential contribution from the organic/aqueous phase boundary,<sup>13</sup>  $R$  is the gas constant,  $F$  is the Faraday constant,  $T$  is the absolute temperature.<sup>7</sup>

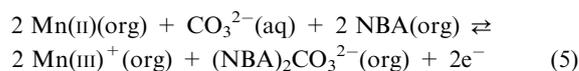


**Fig. 1** (A) Schematic drawing of an organic PPP droplet with  $Mn(III/II)$ , boronic acid  $B$ , and anion  $A^-$  on an electrode surface immersed in aqueous electrolyte. (B) Cyclic voltammograms (scan rate  $50\ mV\ s^{-1}$ ) for  $80\ mM\ TPPMn(III)$  in PPP immersed in  $0.1\ M$  carbonate solution (i–iv) at pH 9.9 with (i) 0, (ii) 0.35, (iii) 0.85, and (iv)  $2.5\ mol\ dm^{-3}$  2-naphthylboronic acid (NBA) and (v) at pH 6. (C) Plot of  $E_{mid}$  potentials versus NBA concentration for (i) pH 9.9 and (ii) pH 6. Theory lines for  $K_{AB} =$  (iii) 10 (iv) 100, (v)  $1000\ mol^{-1}\ dm^3$ .

The shift in the midpoint potential  $\Delta E_{mid}$  obtained from experimental voltammograms is compared to theoretical data (lines) for  $HCO_3^-$  mono-anion transfer in Fig. 1C. Theoretical lines for binding constants  $K_{AB} = 10\ mol^{-1}\ dm^3$  (iii),  $100\ mol^{-1}\ dm^3$  (iv),  $1000\ mol^{-1}\ dm^3$  (v) are shown and a good fit is obtained for  $K_{AB} = 100\ mol^{-1}\ dm^3$ . This binding constant provides a measure for the interaction of  $HCO_3^-$  with the boronic acid in the PPP phase.

At concentrations of 2-naphthylboronic acid of  $0.5\ mol\ dm^{-3}$  and higher a further shift to more negative potentials is observed (as well as coalescence of data for  $CO_3^{2-}$  and

$HCO_3^-$ , see Fig. 1C), which is attributed here to a net double complexation (eqn (5)).



Spreadsheet analysis of this equilibrium involving the dianion and two boronic acids is possible (employing Matlab to solve the resulting cubic equation) but eliminating the cubic term for  $[B_i(oil)] \gg 2[A_i^{2-}(oil)]$  allows an approximate expression for the  $E_{mid}$  shift to be written down (see eqn (6)).

$$E_{rev1/2} = E^0 + \frac{RT}{2F} \ln\left(\frac{c_0}{4}\right) - \frac{RT}{2F} \ln([A_i^{2-}(aq)]) + \Delta E_{mid} \quad (6)$$

with

$$\Delta E_{mid} = \frac{RT}{2F} \ln\left(\frac{1}{[A_i^{2-}(oil)]} \left(-\frac{Y}{2} + \sqrt{\frac{Y^2}{4} - Z}\right)\right)$$

$$Y = \frac{4K_{AB_2}[A_i^{2-}(oil)]^2 - 4K_{AB_2}[B_i(oil)][A_i^{2-}(oil)] + K_{AB_2}[B_i(oil)]^2 + 1}{4K_{AB_2}[B_i(oil)] - 8K_{AB_2}[A_i^{2-}(oil)]}$$

$$Z = \frac{[A_i^{2-}(oil)]}{8K_{AB_2}[A_i^{2-}(oil)] - 4K_{AB_2}[B_i(oil)]}$$

$$K_{AB_2} = \frac{[AB_2^{2-}(oil)]}{[A_i^{2-}(oil)] \times [B(oil)]^2}$$

At high boronic acid concentration, using data points obtained for the facilitated carbonate transfer (eqn (5)) and assuming an estimated transfer potential of the  $CO_3^{2-}$  dianion of ca.  $0.07\ V$  vs. SCE (consistent with di-anionic carboxylates<sup>11</sup>), the dianion binding constant is estimated as  $K_{AB_2} = 2 \times 10^{10}\ mol^{-2}\ dm^6$  consistent with a much stronger binding of the dianion when compared to the mono-anion. The second binding constant can be derived as  $2 \times 10^{10}/100 = 2 \times 10^8\ mol^{-1}\ dm^3$  (compare basicity in water  $K_{B1} = 10^{6.3}\ mol^{-1}\ dm^2$  and  $K_{B2} = 10^{10.3}\ mol^{-1}\ dm^2$  and  $K_{B1} \times K_{B2} = 10^{16.6}\ mol^{-2}\ dm^6$  for carbonate in water<sup>14</sup>).

In conclusion, it has been demonstrated with ion transfer voltammetry experiments that in a pH range from 6 to 11 reversible bicarbonate and carbonate transfer occurs strongly facilitated by 2-naphthylboronic acid. In future, boronic acid containing membranes<sup>15</sup> could be developed to capture or remove bicarbonates and carbonates. Improved boronic acid molecular structures will be possible for further enhancements in bicarbonate and carbonate capture in lipophilic media.

A.M.C. and J.D.W. thank the EPSRC (EP/G002614/1) for financial support.

## Notes and references

† Voltammetric responses recorded with a microAutolab III (Eco Chemie, NL) with a 4.9 mm diameter basal plane pyrolytic graphite (Le Carbon) disc electrode and with a KCl-saturated calomel electrode (SCE) and Pt gauze counter electrode. Microdroplet deposits of PPP were prepared by evaporation of  $MnTPPCL$ , boronic acid, and PPP from acetonitrile.<sup>7</sup>

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