Electronic Supplementary Information for: Detection of *Pseudomonas aeruginosa* quorum sensing molecules at an electrified liquid|liquid micro-interface through facilitated proton transfer.

Edward D. Burgoyne,[a] Andrés F. Molina-Osorio,[a] Reza Moshrefi,[b] Rachel Shanahan,[c] Gerard P. McGlacken,[c] Talia Jane Stockmann, [b,*] and Micheál D. Scanlon [a,*]

[a] The Bernal Institute and Department of Chemical Sciences, School of Natural Sciences, University of Limerick (UL), Limerick V94 T9PX, Ireland
[b] Memorial University of Newfoundland, Chemistry Department, 283 Prince Philip Dr., St. John's, NL Canada A1B 3X7
[c] School of Chemistry and Analytical and Biological Chemistry Research Facility (ABCRF), University College Cork, College Road, Cork, Ireland

*Email: tstockmann@mun.ca (T.J.S)
*Email: micheal.scanlon@ul.ie (M.D.S)

Table of Contents

1. Determination of microchannel radius

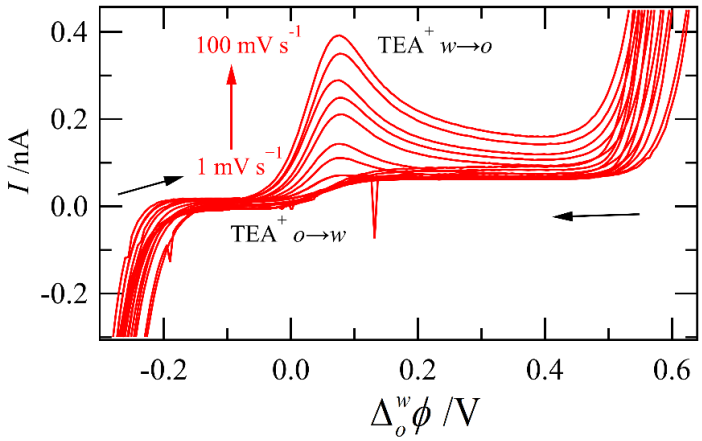

Figure S1: Cyclic voltammograms obtained using Cell S1 and varying the scan rate from 1-100 mV s^{-1}.

Ag	AgCl	0.3 mM TEACl 10 mM LiCl (*aq*)	‖	5 mM BATB (*DCE*)	Sat. BACl 10 mM LiCl (*aq ~ ref.*)	AgCl	Ag		[Cell S1]
Ag	AgCl	0.3 mM NaOBSA 10 mM LiCl (*aq*)	‖	5 mM BATB (*DCE*)	Sat. BACl 10 mM LiCl (*aq ~ ref.*)	AgCl	Ag		[Cell S2]

Figure S1 shows the CVs generated using Cell S1 and by scanning the potential between roughly –0.35 and 0.55 V. During the forward scan (from low to high potentials) a peak-shaped wave was observed with a half-wave potential at 0.049 V.[1] Meanwhile, a steady state or s-shaped wave was observe when scanning from 0.55 V to –0.35 V. Owing to the asymmetric geometry of the capillary, this leads to linear diffusion of ions leaving the pipette (crossing the interface from w→o, egress) and hemispherical diffusion of ions entering the pipette (crossing the interface from o→w, ingress). Therefore, the peak-shaped wave is the transfer of TEA^+ from w→o, while the sigmoidal wave is the ingress of TEA^+ from o→w.

The radius of the microchannel formed at the tip of the pulled borosilicate glass capillary was confirmed using cyclic voltammetric (CV) measurements of the peak-shaped ion transfer wave of tetraethylammonium (TEA^+) from w→o by varying the scan rate (v) as shown in Figure S1 and comparing the change in peak current intensity (i_p) in amperes to the Randles-Sevcik equation[2] below,

$$i_p = 0.4463\left(\frac{F^3}{RT}\right)^{\frac{1}{2}} n^{3/2} A D_{i,\alpha}^{1/2} c_{i,\alpha}^{*} v^{1/2} \qquad [S1]$$

where A, F, R, T, and n are the interfacial surface area, Faraday's constant (96485.33 C mol^{-1}), Universal gas constant (8.314 J mol^{-1} K^{-1}), absolute temperature (298.15 K), and the charge on the ion transferred (+1), respectively. $D_{i,\alpha}$ and $c^*_{i,\alpha}$ are the diffusion coefficient and initial/bulk concentration of species i in phase α. The diffusion coefficient of TEA^+ in water was taken to be 9.8×10^{-6} cm^2 s^{-1}.[3] i_p was plotted against $v^{1/2}$ in Figure S2. Using the slope obtained from linear regression analysis in Figure S2 (dashed line), the radius of the microchannel was calculated to be ~11.9 μm which is within experimental error of the commercially obtained 12.5 μm radius Pt wire used to form the microchannel.

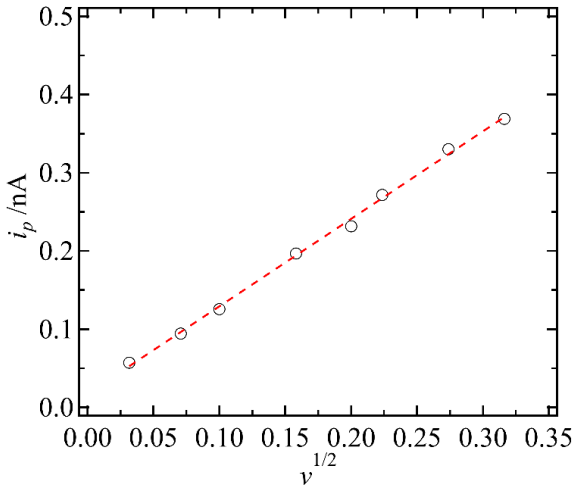

Figure S2: Plot of i_p versus $v^{1/2}$ from Figure S1. Dashed, red curve is the product of linear regression analysis with an R^2 value of 0.998.

2. Asymmetric Diffusion Regime

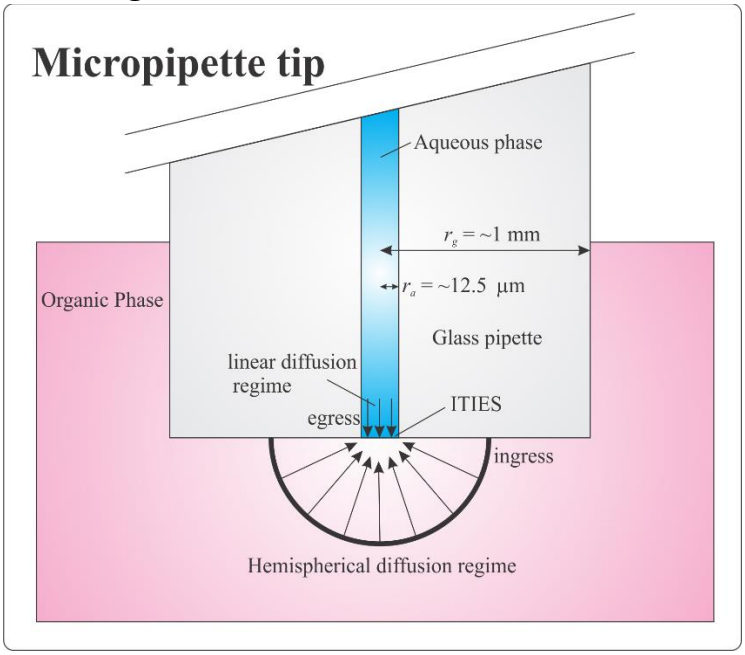

Figure S3: Schematic of the asymmetric diffusion regimes for egress and ingress of material across the ITIES held at the tip of a micropipette with external glass radius (r_g) and an internal microchannel radius (r_a) as indicated.

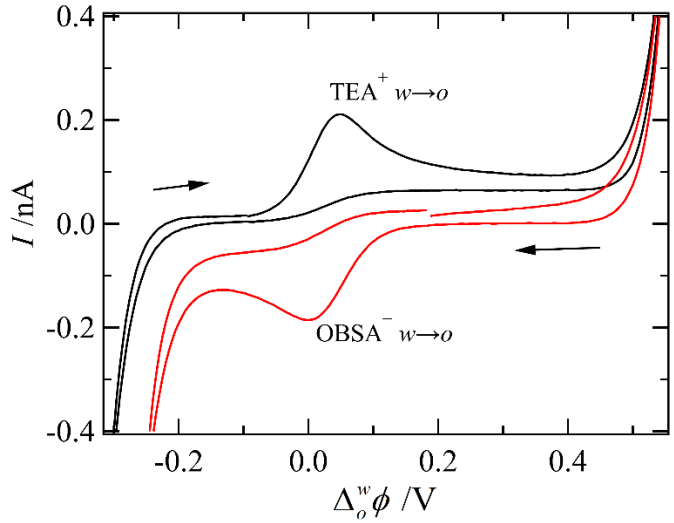

Figure S4: CVs recorded using Cell S1 and S2 with a scan rate of 25 and 50 mV s^{-1} for the black and red trace demonstrating the TEA^+ (tetraethylammonium) and $OBSA^-$ (4-octylbenzenesulfonate) asymmetric ion transfer peak current responses, respectively, based on charge and the pipette geometry as shown in Figure S3.

3. Investigation of proton sources on ligand complexation

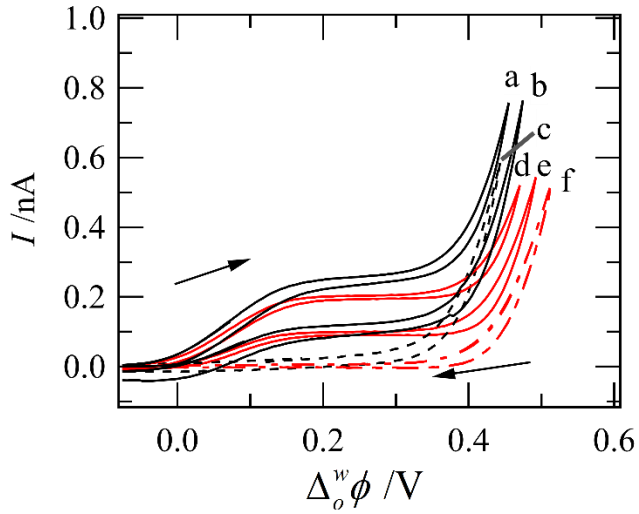

Figure S5: CVs using Cells 1 (curves d, e, f) and 2 (curves a, b, c) with the pH adjusted to 3.5 using HCl and citric acid, respectively, and L = HHQ at 25 (b and e) and 50 μM (a and d). Curves c and f were recorded without HHQ in the DCE phase (blank curves). All other experimental parameters are the same as in Figure 1 of the main text.

4. Cyclic voltammetric response moving from [H⁺]≫[ligand] to the [H⁺]≈[ligand] regime

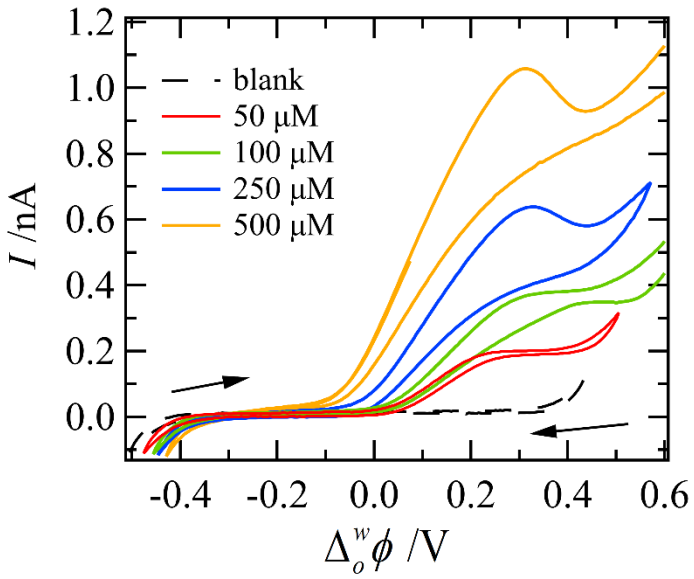

Figure S6: CVs recorded using Cell 1 with *L* = HHQ and [HHQ] varied from 0-500 μM as indicated inset with a scan rate of 25 mV s^{-1}.

5. Linear regression error analysis

The upper and lower associated error with the *line-of-best-fit* (LOBF) was determined using a method described in Skoog *et al*.[4] where the standard deviation (s_c) about the LOBF is defined as,

$$s_c = s_r\sqrt{\frac{1}{N}+\frac{N\left(x-\bar{x}\right)^2}{N\sum x^2-\left(\sum x\right)^2}}$$

where s_r is the standard error from linear regression statistics and the upper and lower error bounds are,

Upper LOBF+ = $y = mx + b + ts_c$

Lower LOBF– = $y = mx + b - ts_c$

In this case, *t* is students *t* value taken from standard tables using a 99.8% confidence interval and *degrees-of-freedom* as defined as N–2, where N is the population or number of data points used to construct the curve.

References

1. Z. Samec, *Pure Appl. Chem.*, 2004, **76**, 2147-2180.
2. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley, New York, 2nd edn., 2001.
3. J. Strutwolf, M. D. Scanlon and D. W. M. Arrigan, *Analyst*, 2009, **134**, 148-158.
4. D. A. Skoog, *Principles of instrumental analysis*, Fourth edition. Fort Worth : Saunders College Pub., [1992] ©1992, 1992.