Supporting Information

Microfluidic droplet-based liquid/liquid extraction modulated by the interfacial Galvani potential difference

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1. Experimental details

1.1 Chemicals

All chemicals of analytical reagent grade were used as received unless mentioned otherwise. The aqueous solution of methyl orange (NaMO) was prepared with ultrapure water (18.2 MΩ cm). Tetramethylammonium chloride (TMACl, 99%), tetra-*n*-butylammonium chloride (TBACl, 97%) were obtained from Aladdin. Tetraethylammonium chloride (TEACl, 98%), tetra-*n*-propylammonium chloride (TPrACl, 99%), bis(triphenylphosphoranylidene)ammonium chloride (BTPPACl, 97%) and 1,2-dichloroethane (DCE) were purchased from Alfa Aesar. Tetraethylammonium tetrakis(4-chlorophenyl)borate (TEATPBCl),

tetra-*n*-propylammonium tetraphenylborate (TPrATPB), tetra-*n*-butylammonium tetraphenylborate (TBATPB) and bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate (BTPPATPFB) were prepared according to a reference method.[1] Bis(triphenylphosphoranylidene)ammonium methyl orange (BTPPAMO) was prepared by 1:1 mixing of BTPPACl and NaMO in water, followed by recrystallization from acetone.

1.2 Measurement of standard transfer potential

The electrochemical measurement of the standard transfer potential of MO^- ($\Delta_o^w \phi_{MO^-}^\ominus$) was performed using an Autolab PGSTAT 302N potentiostat (Utrecht, the Netherlands) with NOVA software at room temperature (25 ± 1 °C). The $\Delta_o^w \phi_{MO^-}^\ominus$ across the water/DCE interface was obtained by a four-electrode liquid/liquid cell with IR drop compensation:

$$\text{Ag} \left| \text{Ag}_2\text{SO}_4 \right| \begin{array}{c} \text{Li}_2\text{SO}_4 \text{ 10 mM} \\ \text{NaMO x mM} \\ \text{TMACl y mM} \\ \text{H}_2\text{O} \end{array} \right\| \begin{array}{c} \text{BTPPATPFB 5 mM} \\ \text{DCE} \end{array} \left| \begin{array}{c} \text{LiCl 10 mM} \\ \text{BTPPACl 1 mM} \\ \text{H}_2\text{O} \end{array} \right| \text{AgCl} \left| \text{Ag} \right.$$

The geometric area of the liquid-liquid interface was 1.53 cm^2. The potential was converted to the Galvani potential difference by cyclic voltammetric measurement of the reversible half-wave potential of the TMA$^+$ cation transfer (0.160 V).[2]

2. Theory

In a typical LLE process of an ionic analyte, the driving force is the distribution coefficient of the analytes between two liquid phases. At equilibrium, one has the equality of the electrochemical potentials of the analyte in the adjacent phases as follows:

$$\overline{\mu}_i^{\,w} = \overline{\mu}_i^{\,o} \tag{1}$$

Further developing yields:

$$\mu_i^{\ominus,w} + RT \ln a_i^w + z_i F \phi^w = \mu_i^{\ominus,o} + RT \ln a_i^o + z_i F \phi^o \tag{2}$$

where $\mu_i^{\ominus,\alpha}(\alpha = o, w)$, R, T, $a_i^{\alpha}(\alpha = o, w)$, z_i, F and $\phi^{\alpha}(\alpha = o, w)$ are the standard chemical potential, the gas constant, the temperature, the activity of the analyte, the valence number of the ion, the Faraday constant and the Galvani potential, respectively. Rearranging eq. 2 gives rise to the Nernst equation:

$$\Delta_o^w \phi = \phi^w - \phi^o = \Delta_o^w \phi_i^{\ominus} + \frac{RT}{z_i F} \ln\left(\frac{a_i^o}{a_i^w}\right) \tag{3}$$

with the standard transfer potential, $\Delta_o^w \phi_i^{\ominus}$, equal to:

$$\Delta_o^w \phi_i^{\ominus} = \frac{\mu_i^{\ominus,o} - \mu_i^{\ominus,w}}{z_i F} \tag{4}$$

An important physical indication of eq. 3 is that when a solution containing ionic solutes is put in contact with another immiscible solution, the ionic solutes will distribute between two phases to establish a Galvani potential difference ($\Delta_o^w \phi$) across the phase boundary, which in turn determines the final concentrations of this ion in each phase. By reorganizing eq. 3, one obtains the distribution coefficient of the ionic analyte (P_i):

$$\ln\left(\frac{a_i^o}{a_i^w}\right) = \ln P_i = \ln P_i^{\ominus} + \frac{z_i F}{RT}\Delta_o^w\phi \tag{5}$$

with the standard distribution coefficient of the ionic analyte ($P_i^{\ominus}$) defined as:

$$\ln P_i^{\ominus} = -\frac{z_i F}{RT}\Delta_o^w\phi_i^{\ominus} \tag{6}$$

In most cases, the extraction systems are complex and contain multiple ionic solutes.

For each ionic solute, eq. 1 can be written, as well as a mass balance equation, *e.g.* for

an ionic solute initially dissolved in water:

$$c_i^o V^o + c_i^w V^w = c_i^0 V^w \tag{7}$$

in which c_i^0, V^w and V^o are the initial concentration of solute i in water, the water

volume and oil volume, respectively. Further taking the electroneutrality condition of

the aqueous phase into account, we obtain:

$$\sum_i z_i F c_i^w = \sum_i \frac{z_i F c_i^0}{1 + \frac{V^o}{V^w}\exp\left[\frac{z_i F}{RT}\left(\Delta_o^w\phi - \Delta_o^w\phi_i^{\ominus\prime}\right)\right]} = 0 \tag{8}$$

in which $\Delta_o^w\phi_i^{\ominus\prime}$ is the formal transfer potential including the activity coefficient

term. Therefore, solving eq. 8 yields the $\Delta_o^w\phi$ across the interface between two

phases, which also determines the equilibrium concentrations of each ionic solute in

two phases. From eq. 8, it can be seen that $\Delta_o^w\phi$ depends on the charge,

concentration and the standard transfer potential of ionic solutes when the volume of

these two phases is equal. As shown in Table S1, dissolving a hydrophilic and a

lipophilic salt featuring the same cation at different concentrations and in the presence

of 2.0 mM NaMO in water initially will determine different $\Delta_o^w\phi$ values at

equilibrium.

Table S1. Interfacial Galvani potential differences tuned by various immiscible electrolyte

solutions featuring a common ion in water phase (W) with 2.0 mM NaMO and in oil phase (O),

respectively.

Phase	Electrolyte	Concentration	$\Delta_o^w \phi$
W	TBACl	5.0	−0.230
O	TBATPB	0.5	
W	TBACl	5.0	−0.204
O	TBATPB	5.0	
W	TBACl	3.0	−0.177
O	TBATPB	5.0	
W	TBACl	2.0	−0.140
O	TBATPB	5.0	
W	TPrACl	5.0	−0.104
O	TPrATPB	1.0	
W	TPrACl	5.0	−0.094
O	TPrATPB	2.3	
W	TPrACl	5.0	−0.089
O	TPrATPB	3.4	
W	TPrACl	5.0	−0.082
O	TPrATPB	5.0	
W	TPrACl	3.4	−0.072
O	TPrATPB	5.0	
W	TPrACl	2.3	−0.062
O	TPrATPB	5.0	
W	TEACl	5.0	−0.031
O	TEATPBCl	0.5	
W	TEACl	5.0	0.019
O	TEATPBCl	5.0	
W	TEACl	0.5	0.078
O	TEATPBCl	5.0	

Two typical $\Delta_o^w \phi$ values at equilibrium calculated by the Wolfram Mathematica software are presented as follows:

(1) The $\Delta_o^w \phi$ value at equilibrium for 2.0 mM NaMO and 5.0 mM TBACl in water phase and 5.0 mM TBATPB in oil phase, respectively:

```
In[1]:=  Exit[];

In[1]:=  Off[Solve::ifun];
         values = {
             R → 8.314,
             F → 96485,
             T → 298,
             CTBATPB → 5,
             CTBACl → 5,
             CNaMO → 2,
             ϕstdTBA → -0.225,
             ϕstdTPB → 0.341,
             ϕstdCl → -0.528,
             ϕstdNa → 0.591,
             ϕstdMO → -0.089
             };
```

$$\text{In[3]:=} \quad CTBAw = CTBAtot \Big/ \left(1 + Exp\left[\frac{F}{RT}(\phi - \phi stdTBA)\right]\right);$$

$$CTPBw = CTPBtot \Big/ \left(1 + Exp\left[\frac{F}{RT}(-\phi + \phi stdTPB)\right]\right);$$

$$CClw = CCltot \Big/ \left(1 + Exp\left[\frac{F}{RT}(-\phi + \phi stdCl)\right]\right);$$

$$CNaw = CNatot \Big/ \left(1 + Exp\left[\frac{F}{RT}(\phi - \phi stdNa)\right]\right);$$

$$CMOw = CMOtot \Big/ \left(1 + Exp\left[\frac{F}{RT}(-\phi + \phi stdMO)\right]\right);$$

```
         CTBAtot = CTBATPB + CTBACl;
         CTPBtot = CTBATPB;
         CCltot = CTBACl;
         CNatot = CNaMO;
         CMOtot = CNaMO;
         equation = CNaw + CTBAw - CClw - CTPBw - CMOw == 0

         phi = FindRoot[equation /. values, {ϕ, 0.4}]
```

$$\text{Out[13]=} \quad -\frac{CTBACl}{1 + e^{\frac{F(-\phi + \phi stdCl)}{RT}}} - \frac{CNaMO}{1 + e^{\frac{F(-\phi + \phi stdMO)}{RT}}} + \frac{CNaMO}{1 + e^{\frac{F(\phi - \phi stdNa)}{RT}}} + \frac{CTBACl + CTBATPB}{1 + e^{\frac{F(\phi - \phi stdTBA)}{RT}}} - \frac{CTBATPB}{1 + e^{\frac{F(-\phi + \phi stdTPB)}{RT}}} == 0$$

$$\text{Out[14]=} \quad \{\phi \to -0.203522\}$$

(2) The $\Delta_o^w\phi$ value at equilibrium for 2.0 mM NaMO and 3.0 mM TBACl in water

phase and 0 mM TBATPB in oil phase, respectively:

```
In[1]:= Exit[];

In[1]:= Off[Solve::ifun];
       values = {
           R → 8.314,
           F → 96485,
           T → 298,
           CTBATPB → 0,
           CTBACl → 3,
           CNaMO → 2,
           φstdTBA → -0.225,
           φstdTPBCl → 0.341,
           φstdCl → -0.528,
           φstdNa → 0.591,
           φstdMO → -0.089
       };

In[3]:= CTBAw = CTBAtot / (1 + Exp[ F/RT (φ - φstdTBA)]);

       CTPBw = CTPBtot / (1 + Exp[ F/RT (-φ + φstdTPB)]);

       CClw = CCltot / (1 + Exp[ F/RT (-φ + φstdCl)]);

       CNaw = CNatot / (1 + Exp[ F/RT (φ - φstdNa)]);

       CMOw = CMOtot / (1 + Exp[ F/RT (-φ + φstdMO)]);

       CTBAtot = CTBATPB + CTBACl;
       CTPBtot = CTBATPB;
       CCltot = CTBACl;
       CNatot = CNaMO;
       CMOtot = CNaMO;
       equation = CNaw + CTBAw - CClw - CTPBw - CMOw == 0

       phiTBA1 = FindRoot[equation /. values, {φ, 0.4}]
```
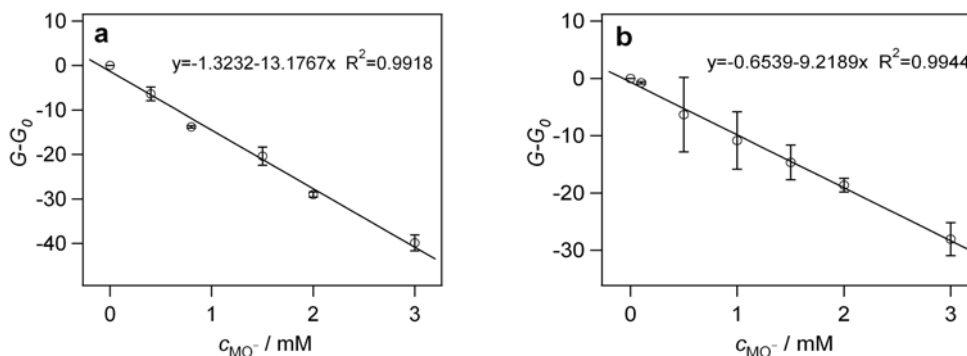
$$
Out[13]= -\frac{CTBACl}{1 + e^{\frac{F(-\phi+\phi stdCl)}{RT}}} - \frac{CNaMO}{1 + e^{\frac{F(-\phi+\phi stdMO)}{RT}}} + \frac{CNaMO}{1 + e^{\frac{F(\phi-\phi stdNa)}{RT}}} + \frac{CTBACl + CTBATPB}{1 + e^{\frac{F(\phi-\phi stdTBA)}{RT}}} - \frac{CTBATPB}{1 + e^{\frac{F(-\phi+\phi stdTPB)}{RT}}} == 0
$$

$$
Out[14]= \{\phi \rightarrow -0.20794\}
$$

3. Calibration curves for both phases

Figure S1 Calibration curves of the proposed system to (a) NaMO in water and (b) BTPPAMO in DCE without adding other electrolytes in both phases, respectively. G and G_0 represent the gray value corresponding to a certain concentration of NaMO in water or of BTPPAMO in DCE, respectively. Flow rate: 0.30 μL min^{-1}.

4. Movies for three typical extraction systems

Movie S1 The extraction of MO$^-$ at the extraction system with $\Delta_o^w \phi$ of -0.203 V (5.0 mM TBACl/5.0 mM TBATPB) at equilibrium. Flow rate: 0.30 μL min^{-1}.

Movie S2 The extraction of MO$^-$ at the extraction system with $\Delta_o^w \phi$ of -0.082 V (5.0 mM TPrACl/5.0 mM TPrATPB) at equilibrium. Flow rate: 0.30 μL min^{-1}.

Movie S3 The extraction of MO$^-$ at the extraction system with $\Delta_o^w \phi$ of -0.031 V (5.0 mM TEACl/0.5 mM TEATPBCl) at equilibrium. Flow rate: 0.30 μL min^{-1}.

References

1. B. Su, J. P. Abid, D. J. Fermin, H. H. Girault, H. Hoffmannova, P. Krtil and Z. Samec, *J. Am. Chem. Soc.*, 2004, **126**, 915-919.
2. T. Wandlowski, V. Marecek and Z. Samec, *Electrochim. Acta*, 1990, **35**, 1173-1175.