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# Ion Transfer Voltammetry by a Simple Two Polarized Interfaces Setup

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Cyclic voltammetry and square wave voltammetry have been used to investigate the transfer of highly hydrophilic ions, including anions and cations, by a simple two polarized interfaces setup. The expression of apparent half-wave potential has been established detailedly by virtue of theory of sampled-current voltammetry involving semi-infinite linear diffusion, which indicates that the property of coupled ion transfer reaction has an effect on the position of the voltammogram on the potential scale. Since the data obtained agree well with literature values, it seems convincing to determine the transfer energies of those highly hydrophilic ions which are very important and have not been reported yet. Then it has been demonstrated as a novel way in combination with sensitive and fast square wave voltammetry for determining the transfer Gibbs energy of complex ions such as miscellaneous inorganic ions.

Ionic solute partitions related to Gibbs transfer energies between two immiscible electrolyte solutions (ITIES), usually water and organic, is a fundamental process in biology and chemistry,<sup>1,2</sup> which underlies many important life functions<sup>3</sup> and technological applications.<sup>4,5</sup> The introduction<sup>6–8</sup> of electrochemistry at the interface between ITIES has led to a significant progress in determining the Gibbs transfer energies and partitions of different miscellaneous inorganic ions and a series of biologically important organic ions and in correlating them to the Galvani potential scale. These parameters allow the quantifying of the

lipophilicity,<sup>9–11</sup> which is important in the design of drugs through the establishment of quantitative structure–activity relationships. The practical application, however, is limited by the potential window of the base electrolytes.<sup>7,8</sup> Typically, only ionic analytes with the formal transfer potential falling in this window can be readily and precisely determined. Moreover, a four-electrode potentiostat has often to be used, which is usually homemade. These two aspects mainly account for the limited practical applications of liquid|liquid interface electrochemistry at this moment.

Over the years, several novel electrochemical methods have been developed to circumvent the problems described above. Supporting interfaces with a micro- or nanodimension on glass pipettes or polymer holes is a significant and successful approach,<sup>12–14</sup> which allows using a commercial three-electrode potentiostat and an electrolyte-free measurement.<sup>15–18</sup> Another successful method<sup>19–25</sup> is based on modifying a solid electrode with one liquid droplet or film immersed in the other immiscible liquid, which has shown particular advantage of studying ions transfer with the conventional three-electrode potentiostat. The so-called three-phase junction electrochemistry<sup>19–21</sup> also provides the possibility to estimate the standard Gibbs free energies of ion transfers without the necessity of putting any supporting electro-

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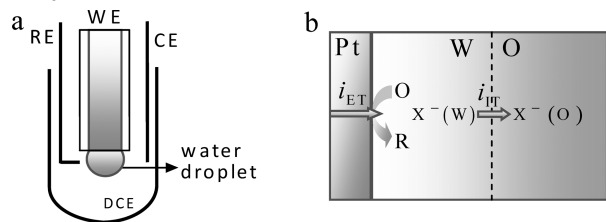
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**Scheme 1. (a) Three-Electrode Cell Used in the Electrochemical Experiments and (b) Mechanism of Ion Transfer at the W/O Interface Limited by the ET at the E/W Interface**



**Scheme 2. Electrochemical Cells (I) and (II) Employed**

Anions  $X^{n-}$ :

Pt | 1 mM  $K_3Fe(CN)_6$  + 1 mM  $K_4Fe(CN)_6$  + 0.1 / n M  $Na_nX$  ||

5 mM BTTPATPBCl | AgTPBCl | Ag

Cell (I)

Cations  $Y^{n+}$ :

Pt | 1 mM  $FeSO_4$  + 1 mM  $Fe_2(SO_4)_3$  + 0.1 / n M  $YCl_n$  ||

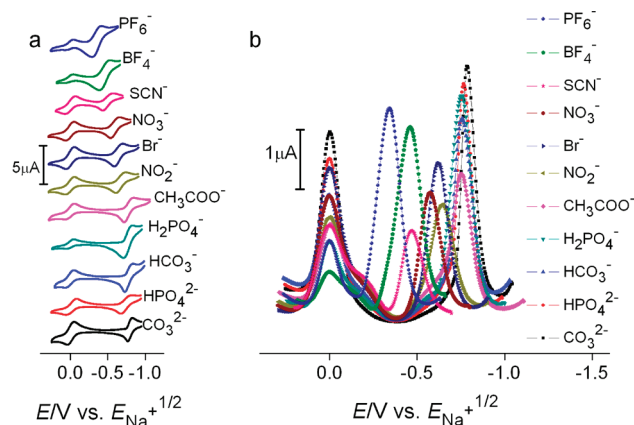
5 mM BTTPATPFB | AgTPFB | Ag

Cell (II)

lyte in the organic phase. Other increasing attention has also been paid to ion transfers in supported liquid membranes,<sup>26–29</sup> where it contains two polarized interfaces in series that is useful for investigating the transfer of highly hydrophilic ions by virtue of a coupled charge transfer reaction.

Although some remarkable progress has been achieved, it is still very challenging to obtain the transfer energies of those highly hydrophilic called extreme ions such as  $Cl^-$ ,  $F^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$ ,  $PO_4^{3-}$ , and  $OH^-$ , and so on. In the present work, we report a simple and accurate method to determine the transfer energies of these extreme ions by renovating the modified electrode approach pioneered by Girault<sup>22,23</sup> and Shao,<sup>24,25</sup> where a specially designed water-droplet was supported onto the surface of a Pt electrode and then dipped into an organic electrolyte as shown in Scheme 1a.

First we would like to explain our reform to Girault and Shao's approach and then clarify the main advantage of studying ion transfer reactions. In Girault and Shao's method, a little target ion with a higher redox couple was dissolved in the droplet, where the overall process is limited by the ion transfer at the water|organic (W|O) interface and thereby nonpolarization occurs at the electrode|water (E|W) interface. In contrast, when a higher concentration of target ion than that of the redox couple was placed in the droplet in our modified approach (as shown in Scheme 2), the overall process becomes limited by the slower mass transfer of electron transfer (ET) at the E|W interface (as illustrated in Scheme 1b). Apparently, this system is comprised of two polarized interfaces, both E|W and W|O interfaces in series. As has been emphatically pointed out by Molina,<sup>28</sup> in this case, the available potential window should be much wider than that traditionally observed, which allows the study of more hydrophilic ions than with systems of a single polarized interface. Furthermore, because of the redox reaction coupled to a corresponding ion transfer at a respective region of potential, it is very convenient



**Figure 1.** (a) CVs obtained with cell (I) at the WIDCE interface, scan rate 0.1 V s<sup>−1</sup>; (b) the corresponding SWVs, scan direction, positive. Detailed technique parameters are included in the Supporting Information.

to calibrate the potential axis by an inner reference regardless of an outer reference in the organic phase.

Figure 1 illustrates the measurements of transfer potentials of various anions using voltammetry with cell (I) in Scheme 2. Obviously, two well-defined current waves were observed along the potential axis. In all cases, the current peak at positive potential was due to the oxidation of ferrocyanide coupled by the transfer of  $K^+$  or  $Na^+$ . Indeed, it should be the transfer of  $Na^+$  not  $K^+$  because of its much higher concentration and their similar thermodynamic property. This has been further confirmed by the observed formal potentials dependence on the concentrations of NaCl (Figure S1), which agrees well with the predication of eq A14. For all the anion transfer measurements, the concentration of  $Na^+$  was kept to be constant at 0.1 M (as shown in Scheme 2), thereby fixing the position of positive wave. This is also in good agreement with the simulation by Ulmeanu et al.,<sup>29</sup> and conveniently we employed it as a reference to calibrate the potential axis as shown in Figure 1. The current wave at negative potential was ascribed to the reduction of ferricyanide coupled to anion transfer, whose position is sensitive to the investigated target anions. Clearly, not only those with known formal transfer potentials or medium hydrophilic anions can be studied, but also with those unknown transfer potentials or highly hydrophilic ions, such as  $F^-$ ,  $OH^-$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$ , and many others, all of which are shown in Figure 1 and Figure S2 in the Supporting Information. Here we use  $ClO_4^-$  ( $\Delta G_{ClO_4}^{tr,w \rightarrow o} = 14.5$  kJ mol<sup>−1</sup>),<sup>30</sup> because of its well-accepted thermodynamic value, as a reference ion to determine the transfer energies of all monovalent anions via the following relationship (see details in the Appendix):

$$\Delta G_X^{tr,w \rightarrow o} = Z_X F \Delta_o^w \phi_X^{tr} \quad (1)$$

$$\Delta_o^w \phi_X^{tr} - \Delta_o^w \phi_{ClO_4}^{tr} = E_X^{1/2} - E_{ClO_4}^{1/2} - \frac{RT}{2F} \ln \frac{D_X^o}{D_{ClO_4}^o} \quad (2)$$

where  $D_X^o$  and  $D_{ClO_4}^o$  are the diffusion coefficients of target ion and reference ion in the organic phase. On the basis of the

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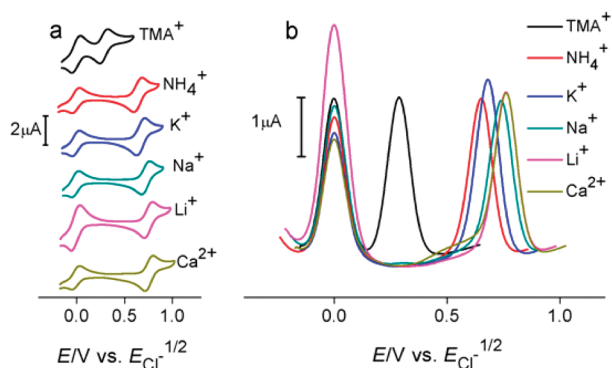
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**Table 1. Apparent Half-Wave Potential and Gibbs Transfer Energies of Anions at the W|DCE Interface**

anion	$E_{1/2}/V^a$	$\Delta G_{tr}^{e',w \rightarrow o}/kJ\ mol^{-1\ b}$	$\Delta G_{tr}^{e',w \rightarrow o}/kJ\ mol^{-1\ c}$
$ClO_4^-$	-0.404		14.5
$PF_6^-$	-0.344	8.7	
$BF_4^-$	-0.443	18.2	17.9
$SCN^-$	-0.532	26.8	26.5
$NO_3^-$	-0.576	31.1	30.3
$Br^-$	-0.620	35.3	35.5
$NO_2^-$	-0.644	37.6	
$Cl^-$	-0.724	45.3	45.1
$Ac^-$	-0.752	48.0	
$H_2PO_4^-$	-0.754	48.2	
$F^-$	-0.756	48.4	
$SO_4^{2-}$	-0.760	97.6	
$HCO_3^-$	-0.763	49.1	
$HPO_4^{2-}$	-0.768	99.2	
$CO_3^{2-}$	-0.784	102.2	
$PO_4^{3-}$	-0.786	153.9	
$OH^-$	-0.798	52.5	

<sup>a</sup> Versus  $E_{Na}^{1/2}$ . <sup>b</sup> Calculated from  $\Delta G_{ClO_4}^{e',w \rightarrow o} = 14.5\ kJ\ mol^{-1}$ . <sup>c</sup> <http://lepa.epfl.ch/cgi/DB/InterrDB.pl>.



**Figure 2.** (a) CVs obtained with cell (II) at the W|DCE interface, scan rate  $0.1\ V\ s^{-1}$ ; (b) the corresponding SWVs, scan direction: positive. Detailed technique parameters are included in the Supporting Information.

Walden rule,  $D_X^o/D_{ClO_4}^o = D_X^w/D_{ClO_4}^w$ , the Gibbs transfer energies of all anions can be calculated by the above equations, all of which are listed in Table 1 and agree well with literature values.<sup>30</sup> This primary experiment thus confirms this measure of validation on the reliability with the present three-electrode approach.

To measure transfer potentials of various cations, we switched to cell (II), as displayed in Scheme 2, where  $K_3Fe(CN)_6$  and  $K_4Fe(CN)_6$  were replaced by  $Fe_2(SO_4)_3$  and  $FeSO_4$  in order to get rid of the interference of  $K^+$ . As shown in Figure 2 and Figure S3 in the Supporting Information, hydrophilic cations including  $H^+$ ,  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  have been examined. The wave at the negative side in this case referred to  $Cl^-$  transfer that on the opposite side was due to cation transfer. In the same way, the transfer potential of  $Cl^-$  was used to calibrate our potential axis, in the condition of keeping its concentration at 0.1 M. In order to evaluate the transfer energies of all univalent cations,  $TMA^+$  ( $\Delta G_{TMA}^{e',w \rightarrow o} = 15.4\ kJ\ mol^{-1}$ )<sup>30</sup> is used as an internal reference by the following equations (see the details in the Appendix):

$$\Delta G_Y^{e',w \rightarrow o} = Z_Y F \Delta_o \phi_Y^{e'} \quad (3)$$

**Table 2. Apparent Half-Wave Potential and Gibbs Transfer Energies of Cations at the W|DCE Interface**

cation	$E_{1/2}/V^a$	$\Delta G_{tr}^{e',w \rightarrow o}/kJ\ mol^{-1\ b}$	$\Delta G_{tr}^{e',w \rightarrow o}/kJ\ mol^{-1\ c}$
$TMA^+$	0.288		15.4
$NH_4^+$	0.652	50.6	51
$K^+$	0.676	52.9	51.5
$Na^+$	0.738	58.9	59.3
$Li^+$	0.748	59.8	58.8
$H^+$	0.756	60.5	56.4
$Mg^{2+}$	0.760	122.0	
$Ca^{2+}$	0.764	122.8	

<sup>a</sup> Versus  $E_{Cl}^{1/2}$ . <sup>b</sup> Calculated from  $\Delta G_{TMA}^{e',w \rightarrow o} = 15.4\ kJ\ mol^{-1}$ . <sup>c</sup> <http://lepa.epfl.ch/cgi/DB/InterrDB.pl>.

$$\Delta_o \phi_Y^{e'} - \Delta_o \phi_{TMA}^{e'} = E_Y^{1/2} - E_{TMA}^{1/2} + \frac{RT}{2F} \ln \frac{D_Y^o}{D_{TMA}^o} \quad (4)$$

where  $D_Y^o$  and  $D_{TMA}^o$  are the diffusion coefficients of the target ion and the reference ion in the organic phase, respectively. All values thus estimated are included in Table 2, which are also consistent with the literature values.<sup>30</sup> Knowing the transfer energies of  $OH^-$  and  $H^+$  (Tables 1 and 2), the dissociation constant of water in DCE can be calculated as  $6.7 \times 10^{-34}$  by eq 5, which is consistent with the reported value of  $5.6 \times 10^{-34}$ .<sup>31</sup>

$$\Delta G_{diss,water}^{DCE} = \Delta G_{diss,water}^{water} + \Delta G_{tr,H^+}^{e',w \rightarrow DCE} + \Delta G_{tr,OH^-}^{e',w \rightarrow DCE} - \Delta G_{tr,water}^{e',w \rightarrow DCE} \quad (5)$$

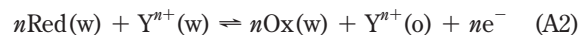
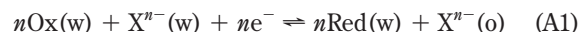
where  $\Delta G_{tr,water}^{e',w \rightarrow DCE}$  is the transfer energies of  $H_2O$  across the W|DCE interface,  $15.4\ kJ\ mol^{-1}$ .<sup>32</sup>  $\Delta G_{diss,water}^{water}$  is the energies of dissociation of water in the aqueous phase.  $\Delta G_{diss,water}^{DCE}$  is the energies of dissociation of water in the organic phase.

In conclusion, this simple three-electrode approach has manifested itself to be simple but useful method for determining the Gibbs transfer energies of ions at liquid/liquid interfaces, particularly toward highly hydrophilic ions. We believe that this methodology is not only technologically interesting but also fundamentally important owing to simulation of the permeation of ions across the cell membrane energetically driven and limited by redox transformations. Additionally, we can also foresee diverse possibilities of extending this approach to other complex ions such as miscellaneous inorganic ions and a series of biologically important organic ions, other organic media such as biological mimics that use octanol, ionic liquids, and many others.

## ACKNOWLEDGMENT

The authors are most grateful to the NSFC (Grant No. 20827004) and to the Department of Science and Technology of Jilin Province (Grant No. 20080518) for the financial supports. B. S. also gratefully acknowledges the financial support by the Fundamental Research Funds for the Central Universities (Grant 2009QNA3012) and ZJU.

## APPENDIX



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On the basis of our experiments, two pairs of peaks corresponding to above reactions were demonstrated clearly at each side of potential, which implies that the redox couple can have a separate existence to take part in the respective coupled reaction. Because of a much higher concentration of target ion than that of the redox couple in the droplet, the overall process is limited by the slower mass transfer of the ET step. In this case, the surface concentration of the target ion in the aqueous phase can be taken approximately as the same as its initial bulk concentration. Provided that all the charge transfer processes are fast enough to establish the Nernst equilibrium, the potential difference at each interface corresponding to eq A1 can be given by

$$E = \Delta_o^{\text{Pt}}\phi + E_{\text{ref}}^{\circ} \quad (\text{A3})$$

$$\Delta_o^{\text{Pt}}\phi = \Delta_w^{\text{Pt}}\phi + \Delta_o^{\text{w}}\phi \quad (\text{A4})$$

$$\Delta_w^{\text{Pt}}\phi = \Delta_w^{\text{Pt}}\phi_{\text{et}}^{\circ} + \frac{RT}{F} \ln \sqrt{\frac{D_{\text{Red}}^{\text{w}}}{D_{\text{Ox}}^{\text{w}}}} + \frac{RT}{F} \ln \frac{I_{\text{lc}} - I}{I} \quad (\text{A5})$$

$$\Delta_o^{\text{w}}\phi = \Delta_o^{\text{w}}\phi_X^{\circ} - \frac{RT}{nF} \ln \frac{c_X^{\circ}}{c_X^{\text{w},0}} \quad (\text{A6})$$

where  $E$  is the externally polarized potential,  $E_{\text{ref}}^{\circ}$  is the reference potential in the organic phase,  $\Delta_w^{\text{Pt}}\phi_{\text{et}}^{\circ}$  and  $\Delta_o^{\text{w}}\phi_X^{\circ}$  are the formal potentials of the redox couple and target ion  $X^{n-}$ .  $c_X^{\circ}$  and  $c_X^{\text{w},0}$  are the surface concentration of target ion  $X^{n-}$  in the organic phase and its initial bulk concentration in the aqueous phase.  $D_{\text{Red}}^{\text{w}}$  and  $D_{\text{Ox}}^{\text{w}}$  are the diffusion coefficients of the redox couple in the aqueous phase.  $I$  and  $I_{\text{lc}}$  are the sampled current and the sampled cathodic limiting current of eq A1.

Considering the initial condition of concentration of system, the sampled-current  $I$  flowing through each interface is equivalent and expressed by

$$I = nFA_1 \sqrt{\frac{D_X^{\circ}}{\pi\tau}} c_X^{\circ} \quad (\text{A7})$$

$$I_{\text{lc}} = FA_2 \sqrt{\frac{D_{\text{Ox}}^{\text{w}}}{\pi\tau}} c_{\text{Ox}}^{\text{w},0} \quad (\text{A8})$$

where  $D_X^{\circ}$  is the diffusion coefficient of  $X^{n-}$  in the organic phase.  $c_{\text{Ox}}^{\text{w},0}$  is the initial bulk concentration of Ox in the aqueous phase.  $\tau$  is the sampling time for sampled-current voltammetry.  $A_1$ ,  $A_2$  are the surface areas of the droplet and the area of the solid electrode. As shown in Scheme 1a, we assumed that the droplet is hemispheric, thus  $A_1/A_2 = 2$ .

By solving eqs A7 and A8, we obtain

$$c_X^{\circ} = \frac{Ic_{\text{Ox}}^{\text{w},0}\sqrt{D_{\text{Ox}}^{\text{w}}}}{2nI_{\text{lc}}\sqrt{D_X^{\circ}}} \quad (\text{A9})$$

Substituting eqs A4–A6 and A9 into eq A3, it becomes

$$E = \Delta_w^{\text{Pt}}\phi_{\text{et}}^{\circ} + \Delta_o^{\text{w}}\phi_X^{\circ} + \frac{RT}{F} \ln \sqrt{\frac{D_{\text{Red}}^{\text{w}}}{D_{\text{Ox}}^{\text{w}}}} + \frac{RT}{F} \ln \frac{I_{\text{lc}} - I}{I} + \frac{RT}{nF} \ln \frac{2nI_{\text{lc}}c_X^{\text{w},0}(D_X^{\circ})^{1/2}}{Ic_{\text{Ox}}^{\text{w},0}(D_{\text{Ox}}^{\text{w}})^{1/2}} + E_{\text{ref}}^{\circ} \quad (\text{A10})$$

When  $I = I_{\text{lc}}/2$  and  $D_{\text{Ox}}^{\text{w}} = D_{\text{Red}}^{\text{w}}$ ,

$$E_{1/2} = \Delta_w^{\text{Pt}}\phi_{\text{et}}^{\circ} + \Delta_o^{\text{w}}\phi_X^{\circ} + \frac{RT}{nF} \ln \frac{4nc_X^{\text{w},0}(D_X^{\circ})^{1/2}}{c_{\text{Ox}}^{\text{w},0}(D_{\text{Ox}}^{\text{w}})^{1/2}} + E_{\text{ref}}^{\circ} \quad (\text{A11})$$

Employing  $\text{ClO}_4^-$  as an inner reference, the transfer potential of  $X^{n-}$  can be calculated by

$$\Delta_o^{\text{w}}\phi_X^{\circ} - \Delta_o^{\text{w}}\phi_{\text{ClO}_4}^{\circ} = E_X^{1/2} - E_{\text{ClO}_4}^{1/2} - K_1$$

$$K_1 = \frac{RT}{2nF} \ln \frac{D_X^{\circ}(D_{\text{Ox}}^{\text{w}})^{n-1}}{(D_{\text{ClO}_4}^{\circ})^n} + \frac{RT}{nF} \ln \frac{nc_X^{\text{w},0}(c_{\text{Ox}}^{\text{w},0})^{n-1}}{4^{n-1}(c_{\text{ClO}_4}^{\text{w},0})^n} \quad (\text{A12})$$

When  $n = 1$ , it can be simplified as

$$\Delta_o^{\text{w}}\phi_X^{\circ} - \Delta_o^{\text{w}}\phi_{\text{ClO}_4}^{\circ} = E_X^{1/2} - E_{\text{ClO}_4}^{1/2} - \frac{RT}{2F} \ln \frac{D_X^{\circ}}{D_{\text{ClO}_4}^{\circ}} \quad (\text{A13})$$

On the basis of the same principle, we obtain the relationship of half-wave potential of eq A2,

$$E_{1/2} = \Delta_w^{\text{Pt}}\phi_{\text{et}}^{\circ} + \Delta_o^{\text{w}}\phi_Y^{\circ} + \frac{RT}{nF} \ln \frac{c_{\text{Red}}^{\text{w},0}(D_{\text{Red}}^{\text{w}})^{1/2}}{4nc_Y^{\text{w},0}(D_Y^{\circ})^{1/2}} + E_{\text{ref}}^{\circ} \quad (\text{A14})$$

In this time, treating  $\text{TMA}^+$  as an inner reference, the transfer potential of  $Y^{n+}$  should be estimated by

$$\Delta_o^{\text{w}}\phi_Y^{\circ} - \Delta_o^{\text{w}}\phi_{\text{TMA}}^{\circ} = E_Y^{1/2} - E_{\text{TMA}}^{1/2} - K_2$$

$$K_2 = \frac{RT}{2nF} \ln \frac{(D_{\text{TMA}}^{\circ})^n}{D_Y^{\circ}(D_{\text{Red}}^{\text{w}})^{n-1}} + \frac{RT}{nF} \ln \frac{4^{n-1}(c_{\text{TMA}}^{\text{w},0})^n}{nc_Y^{\text{w},0}(c_{\text{Red}}^{\text{w},0})^{n-1}} \quad (\text{A15})$$

When  $n = 1$ , it can be defined by

$$\Delta_o^{\text{w}}\phi_Y^{\circ} - \Delta_o^{\text{w}}\phi_{\text{TMA}}^{\circ} = E_Y^{1/2} - E_{\text{TMA}}^{1/2} + \frac{RT}{2F} \ln \frac{D_Y^{\circ}}{D_{\text{TMA}}^{\circ}} \quad (\text{A16})$$

## SUPPORTING INFORMATION AVAILABLE

Experimental details and other ion transfer voltammograms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Received for review July 28, 2010. Accepted August 8, 2010.

AC102010B