SUPPORTING INFORMATION

Potential-Dependent Adsorption of Amphoteric Rhodamine Dyes at the Oil/Water Interface as Studied by Potential-Modulated Fluorescence Spectroscopy

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Derivation of eq 3

For the sake of simplicity, we made the following assumptions: (a) The pH of the aqueous phase is adjusted with an appropriate buffer or a strong acid so that the acid dissociation equilibrium for R^+ is always established. (b) The interfacial transfers of R^+ and R^{\pm} are so fast that distribution equilibrium is established for their interfacial concentrations in both phases. (c) The sole transfer of H^+ across the interface is negligible in the potential range studied, though H^+ can transfer at the interface through complexation with R^{\pm} . (d) Neither R^+ nor R^{\pm} forms any ion pair with supporting-electrolyte ions in both phases.

Based on assumption (a), we have a different expression for eq 4:

$$K_1 = \frac{c_{R^+}}{c_{R^+}}$$
(S1)

where c_j denotes the concentration of species $j (= R^+ \text{ or } R^{\pm})$ in the aqueous phase. In this supplementary information, the super- or subscript "o" represents the organic phase and no super- or subscript the aqueous phase. Also, all equilibrium constants are defined with concentrations (not the activities).

The diffusion problem of $R^{\scriptscriptstyle +}$ and $R^{\scriptscriptstyle \pm}$ in the aqueous phase can be expressed using the total concentration

$$c_{t} = c_{R^{+}} + c_{R^{\pm}}$$
(S2)

and the effective diffusion coefficient \overline{D} (= \overline{D}^{W} defined by eq 6), as

$$\frac{\partial c_{t}}{\partial t} = \overline{D} \frac{\partial^{2} c_{t}}{\partial x^{2}}$$
(S3)

Here, *t* and *x* show the time and the position (for the coordinate, see Figure 3), respectively. The initial condition (at t = 0) for the partial differential equation, eq S3, is

$$c_{\rm t} = c_{\rm t}^* \tag{S4}$$

where c_t^* is the total bulk concentration of the rhodamine in the aqueous phase. The boundary condition is

$$c_{t} \to c_{t}^{*} \ (x \to +\infty) \tag{S5}$$

In addition, the total flux of the rhodamine species at the interface on the aqueous-phase side is given by

$$f_{t} = \overline{D} \left(\frac{\partial c_{t}}{\partial x} \right)_{x=0}$$
(S6)

By solving eq S3 under the conditions of eqs S4–S6 by Laplace transformation, we have the following equation:

$$\left(c_{t}\right)_{x=0} = c_{t}^{*} - \frac{1}{\sqrt{\pi \overline{D}}} \int_{0}^{t} \frac{f_{t}(u)}{\sqrt{t-u}} \mathrm{d}u$$
(S7)

On the other hand, the diffusions of the rhodamine species in the organic phase are treated separately:

$$\frac{\partial c_j^{\rm o}}{\partial t} = D_j^{\rm o} \frac{\partial^2 c_j^{\rm o}}{\partial x^2} \quad (j = {\rm R}^+, {\rm R}^\pm)$$
(S8)

Although the acid association/dissociation ($R^+ \leftrightarrows R^{\pm} + H^+$) occurs in the organic phase, its contribution to the rate of concentration change, $\partial c_j^0 / \partial t$, can be neglected, provided that the reaction is in equilibrium at any place in the organic phase. The initial condition (at t = 0) for eq S8 is

$$c_i^0 = 0 \ (j = \mathbf{R}^+, \mathbf{R}^\pm)$$
 (S9)

and the boundary condition at $x \rightarrow -\infty$ is

$$c_j^0 \to 0 \ (j = \mathbb{R}^+, \mathbb{R}^\pm) \tag{S10}$$

In addition, the fluxes of the rhodamine species at the interface on the organicphase side are given by

$$f_j^{O} = D_j^{O} \left(\frac{\partial c_j^{O}}{\partial x} \right)_{x=0} \quad (j = \mathbb{R}^+, \mathbb{R}^\pm)$$
(S11)

By solving eq S8 under these conditions by Laplace transformation, we have the following equation:

$$\left(c_{j}^{O}\right)_{x=0} = \frac{1}{\sqrt{\pi D_{j}^{O}}} \int_{0}^{t} \frac{f_{j}^{O}(u)}{\sqrt{t-u}} du \quad (j = \mathbb{R}^{+}, \mathbb{R}^{\pm})$$
(S12)

For simplicity, it is here assumed that the adsorption amounts of the rhodamine species at the interface are not varied with time, so that

$$f_{t} = f_{R^{+}}^{0} + f_{R^{\pm}}^{0}$$
(S13)

Using eqs S7, S12, and S13, we obtain

$$\sqrt{\overline{D}}\left\{c_{t}^{*}-\left(c_{t}\right)_{x=0}\right\}=\sqrt{D_{R^{*}}^{O}}\left(c_{R^{*}}^{O}\right)_{x=0}+\sqrt{D_{R^{*}}^{O}}\left(c_{R^{*}}^{O}\right)_{x=0}$$
(S14)

Based on assumption (b), the distribution of R^+ at the O/W interface is expressed by the Nernst equation:

$$K_{\mathbf{R}^{+}} = \frac{\left(c_{\mathbf{R}^{+}}^{\mathrm{O}}\right)_{x=0}}{\left(c_{\mathbf{R}^{+}}\right)_{x=0}} = \exp\left\{\frac{F}{RT}\left(\Delta_{\mathrm{O}}^{\mathrm{W}}\phi - \Delta_{\mathrm{O}}^{\mathrm{W}}\phi_{\mathbf{R}^{+}}^{\circ}\right)\right\}$$
(S15)

Regarding the neutral species R^{\pm} , the distribution coefficient is independent of $\Delta_{O}^{W}\phi$:

$$K_{\rm D} = \frac{\left(c_{\rm R^{\pm}}^{\rm O}\right)_{x=0}}{\left(c_{\rm R^{\pm}}\right)_{x=0}} \tag{S16}$$

Substituting eqs S15 and S16 into eq S14 yields

$$\sqrt{\overline{D}}\left\{c_{t}^{*}-\left(c_{t}\right)_{x=0}\right\}=\sqrt{D_{R^{*}}^{O}}K_{R^{*}}\left(c_{R^{*}}\right)_{x=0}+\sqrt{D_{R^{*}}^{O}}K_{D}\left(c_{R^{*}}\right)_{x=0}$$
(S17)

Since the interfacial concentrations of R^+ and R^{\pm} are expressed as

$$\left(c_{R^{+}}\right)_{x=0} = \frac{K_{1}}{1+K_{1}} \left(c_{t}\right)_{x=0}$$
(S18)

$$\left(c_{R^{\pm}}\right)_{x=0} = \frac{1}{1+K_{1}} \left(c_{t}\right)_{x=0}$$
(S19)

we can obtain the total concentration at the interface from eq S17 as

$$(c_{t})_{x=0} = c_{t}^{*} \left\{ 1 + \sqrt{\frac{D_{R^{*}}^{O}}{\overline{D}}} \left(\frac{K_{1}}{1+K_{1}} \right) K_{R^{*}} + \sqrt{\frac{D_{R^{*}}^{O}}{\overline{D}}} \left(\frac{1}{1+K_{1}} \right) K_{D} \right\}^{-1}$$
 (S20)

Under potentiostatic conditions, K_{R^+} is constant at a given potential (see eq S15), so that by using eq S20, time-independent $(c_t)_{x=0}$ can be obtained. Accordingly, we can then obtain $(c_{R^+})_{x=0}$ and $(c_{R^\pm})_{x=0}$ from $(c_t)_{x=0}$ using eqs S18 and S19, from which time-independent $(c_{R^+}^0)_{x=0}$ and $(c_{R^\pm}^0)_{x=0}$ can be obtained using eqs S15 and S16. The interfacial concentrations of R^+ and R^\pm on the organic-phase side are thus time independent under potentiostatic conditions, therefore the Laplace transform $(L\{f_j^{0}(t)\} = \overline{f}_j^{0}(s))$ of eq S12 yields

$$\bar{f}_{j}^{O}(s) = \sqrt{D_{j}^{O}} \frac{\left(c_{j}^{O}\right)_{x=0}}{\sqrt{s}} \quad (j = R^{+}, R^{\pm})$$
 (S21)

The inverse Laplace transformation yields

$$f_{j}^{0}(t) = \sqrt{D_{j}^{0}} \frac{\left(c_{j}^{0}\right)_{x=0}}{\sqrt{\pi t}} \quad (j = R^{+}, R^{\pm})$$
(S22)

Taking into account assumption (c), we can write the current density i(t) as

$$i(t) = F f_{\mathsf{R}^+}^{\mathsf{O}}(t) \tag{S23}$$

Introducing eq S22 for $j = R^+$ into eq S23 yields

$$i(t) = F \sqrt{D_{R^+}^{O}} \frac{\left(c_{R^+}^{O}\right)_{x=0}}{\sqrt{\pi t}}$$
(S24)

Because $(c_{R^+}^{O})_{x=0}$ in this equation is given by eqs S15, S18, and S20, we obtain the following expression for i(t):

$$i(t) = \left(\frac{K_{1}}{1+K_{1}}\right) \frac{F\sqrt{D_{R^{+}}^{O}}c_{t}^{*}}}{\left[\left\{1+\sqrt{\frac{D_{R^{+}}^{O}}{\overline{D}}}\left(\frac{1}{1+K_{1}}\right)K_{D}\right\}\left(K_{R^{+}}\right)^{-1} + \sqrt{\frac{D_{R^{+}}^{O}}{\overline{D}}}\left(\frac{K_{1}}{1+K_{1}}\right)\right]\sqrt{\pi t}}$$
(S25)

The limiting current density $i_{\text{lim}}(t)$ should be obtained by setting $K_{R^+} \rightarrow +\infty$ (i.e., $\Delta_0^W \phi \rightarrow +\infty$):

$$i_{\rm lim}(t) = \frac{F\sqrt{\overline{D}}c_{\rm t}^*}{\sqrt{\pi t}}$$
(S26)

Using eqs S15, S25, and S26, an expression for the polarographic or steady state current–potential curve is obtained:

$$\begin{split} \Delta_{O}^{W}\phi &= \Delta_{O}^{W}\phi_{R^{+}}^{\circ} + \frac{RT}{F}\ln\sqrt{\frac{\overline{D}}{D_{R^{+}}^{O}}} - \frac{RT}{F}\ln\left(\frac{K_{1}}{1+K_{1}}\right) + \frac{RT}{F}\ln\left\{1 + \sqrt{\frac{D_{R^{\pm}}^{O}}{\overline{D}}}\left(\frac{1}{1+K_{1}}\right)K_{D}\right\} \\ &+ \frac{RT}{F}\ln\frac{i(t)}{i_{\lim}(t) - i(t)} \end{split}$$
(S27)

By setting $i(t) = i_{\text{lim}}(t)/2$ in this equation, we finally obtain eq 3 for the reversible half-wave potential, $\Delta_0^W \phi_{1/2}^r$.

Curve fitting for the frequency dependence of the PMF response

The frequency dependence of the PMF response for RB (Figure 5) was analyzed by taking into account (1) the effect of uncompensated IR drop and (2) the contribution from the ion-transfer response.

(1) The effect of uncompensated IR drop

A conventional equivalent circuit for charge transfer across the interface was assumed:



Here, R_u is the uncompensated solution resistance, C_{dl} is the interfacial capacitance, R_b is the transfer resistance for the supporting electrolyte, and Z_f is the faraday impedance of the reaction given by eq 8, which is expressed as the sum of the charge-transfer resistance (R_{ct}) and the Warburg impedance (Z_W):

$$Z_{\rm f} = R_{\rm ct} + Z_{\rm W} = R_{\rm ct} + (1-{\rm i})\sigma\omega^{-1/2}$$
 with ${\rm i} = (-1)^{1/2}$ (S28)

where R_{ct} is a function of z, c_0 , the ion-transfer rate constant (k_t) , and the interfacial area (S), and σ is a function of z, c_0 , $\Delta_0^W \phi$, $\Delta_0^W \phi_{R^+}^\circ$, and the diffusion coefficient of R^{\pm} in the organic phase $(D_{R^{\pm}}^0)$ (cf. eqs 27 and 28 in ref. 18). The total impedance is then given by $Z_T = R_u + \left[i\omega C_{dl} + \frac{1}{R_b} + \frac{1}{R_{ct} + (1-i)\sigma\omega^{-1/2}}\right]^{-1}$ (S29)

$$\Delta_{\rm O}^{\rm W}\phi_{\rm l}^{\rm eff} = \Delta_{\rm O}^{\rm W}\phi_{\rm l,\,re}^{\rm eff} + i\,\Delta_{\rm O}^{\rm W}\phi_{\rm l,\,im}^{\rm eff} = \Delta_{\rm O}^{\rm W}\phi_{\rm l} \left[1 - \frac{R_{\rm u}}{Z_{\rm T}}\right]$$
(S30)

Considering such *ac* potential attenuation, the modified expression for the adsorption response is described as follows:

$$\Delta F_{a, re}^{O} = -C_{a} \left[\frac{\left\{ k_{a,0} c_{0} \alpha (1 - \theta_{0}) - k_{d,0} (\alpha - 1) \theta_{0} \right\} \left\{ \Delta_{O}^{W} \phi_{1, re}^{eff} (k_{a,0} c_{0} + k_{d,0}) + \Delta_{O}^{W} \phi_{1, im}^{eff} \omega \right\}}{\left(k_{a,0} c_{0} + k_{d,0} \right)^{2} + \omega^{2}} \right]$$
(S31)

$$\Delta F_{a, im}^{O} = C_{a} \left[\frac{\left\{ k_{a,0} c_{0} \alpha (1 - \theta_{0}) - k_{d,0} (\alpha - 1) \theta_{0} \right\} \left\{ \Delta_{O}^{W} \phi_{1, re}^{eff} \omega - \Delta_{O}^{W} \phi_{1, im}^{eff} \left(k_{a,0} c_{0} + k_{d,0} \right) \right\}}{\left(k_{a,0} c_{0} + k_{d,0} \right)^{2} + \omega^{2}} \right]$$
(S32)

(2) The contribution from the ion-transfer response

It is assumed that the observed real and imaginary components of the PMF response are expressed as

$$\Delta F_{\rm re} = \Delta F_{\rm a, re}^{\rm O}' + \mathbf{a} \Delta F'_{\rm t, re}$$
(S33)

$$\Delta F_{\rm im} = \Delta F_{\rm a,im}^{\rm O}' + \mathbf{a} \,\Delta F'_{\rm t,\,im} \tag{S34}$$

where the fitting parameter **a** is related to the relative contribution of the ion-transfer response in the present experimental setup, and $\Delta F'_{t,re}$ and $\Delta F'_{t,im}$ stand for the real and imaginary components of the PMF response for the ion transfer with *ac* potential attenuation, which are given by¹⁸

$$\Delta F'_{t, re} = C_t \left[\frac{\Delta_0^W \phi_{1, re}^{eff} \sigma \omega^{-3/2} + \Delta_0^W \phi_{1, im}^{eff} (R_{ct} + \sigma \omega^{-1/2}) \omega^{-1}}{(R_{ct} + \sigma \omega^{-1/2})^2 + (\sigma \omega^{-1/2})^2} \right]$$
(S35)

$$\Delta F'_{t, im} = -C_t \left[\frac{\Delta_0^W \phi_{l, re}^{eff} (R_{ct} + \sigma \omega^{-1/2}) \omega^{-1} - \Delta_0^W \phi_{l, im}^{eff} \sigma \omega^{-3/2}}{(R_{ct} + \sigma \omega^{-1/2})^2 + (\sigma \omega^{-1/2})^2} \right]$$
(S36)

Here, C_t is a constant including optical properties of the transferring species and conditional factor such as the angle of incidence of the excitation beam.

Using eqs 10, 11, and S29–S36, a least-square curve fitting was performed for the PMF complex plane shown in Figure 5. For the curve fitting, we set parameters as follows: z = +1, $\alpha = 0.5$, $b^{O} = 0.5$, $k_t = 0.1$ cm s⁻¹, $D_{R^{\pm}}^{O} = 5 \times 10^{-6}$ cm² s⁻¹, $R_u = 350 \Omega$, $R_b =$ 40 k Ω , $C_{dl} = 5 \times 10^{-6}$ F, and S = 0.5 cm².



Figure S1. Emission spectra of (A) RB and (B) R19 in DCE solutions: (—) DCE containing 5 mM BTPPATClPB, into which 1.0×10^{-5} R[±] was totally extracted from the aqueous solution (unbuffered); (—) DCE containing 1.0×10^{-5} R⁺TClPB⁻ (this salt was prepared by metathesis of R⁺Cl⁻ and K⁺TClPB⁻). Excitation wavelength: 532 nm. It seems that the amphoteric form of R19 is mostly transformed to the colorless lactone form.



Figure S2. Potential dependences of the PMF response for R19 at (A) pH 6.8 and (B) pH 3.0. R19 was initially added to the aqueous phase³⁸ at the concentration of 1.0×10^{-5} M. The solid and dashed curves represent the real and imaginary components of the PMF signals, respectively. The excitation and detected emission wavelengths were 532 nm and 548 nm, respectively. The vertical dashed line indicates the ion-transfer potential.