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## Interfacial behavior of sulforhodamine 101 at the polarized water/1,2-dichloroethane interface studied by spectroelectrochemical techniques

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**Abstract** The transfer mechanism of an amphoteric rhodamine, sulforhodamine 101 (SR101), across the polarized water/1,2-dichloroethane (DCE) interface was investigated using cyclic voltammetry, differential volt-fluorometry and potential-modulated fluorescence (PMF) spectroscopy. The voltammetric response for the ion transfer of SR101 monoanion from water to DCE was observed as the diffusion-controlled transfer process. An unusual voltammetric response was found at 0.15 V more negative than the formal transfer potential of  $\text{SR101}^- (\Delta_{\text{O}}^{\text{W}} \phi^{\circ})$  in the cyclic voltammogram and volt-fluorogram. The frequency dependence of the PMF responses confirmed the presence of the adsorption processes at negative potentials. In addition, a further transient adsorption step was uncovered at  $\Delta_{\text{O}}^{\text{W}} \phi^{\circ}$ . The interfacial mechanism of SR101 is discussed by comparing the results obtained from each technique.



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**Keywords** Sulforhodamine 101 · Adsorption · Liquid/liquid interface · Potential modulated fluorescence

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### Introduction

The elucidation of the interfacial mechanism in the liquid/liquid system is a fundamental problem of modern analytical and bioanalytical chemistry in order that phase-transfer kinetics, heterogeneous electron transfer, self-assembly of surfactants, and interfacial catalysis can be understood [1, 2]. Ion-transfer processes across liquid/liquid interfaces can be described in terms of a series of elementary steps involving transport phenomena and specific adsorption at the interfacial region. The analysis of electrochemical responses in the presence of surface-active species is complicated due to the primitive understanding of the potential distribution across the interface. Considerable efforts have been devoted to accessing the potential dependence of adsorption by means of spectroscopic techniques such as surface second-harmonic generation [3–6] and potential-modulated spectroscopy [7–10]. Potential-modulated fluorescence (PMF) spectroscopy has provided detailed information on the dynamics of charge transfer and adsorption as a function of the Galvani potential difference across the liquid/liquid interface. In this technique, a sinusoidal potential modulation is superimposed on

the DC bias generating a periodic perturbation of the dye concentration at the interface. The AC surface concentration manifests itself as a modulated fluorescence signal that can be measured by phase-sensitive detection. The dependency of the amplitude and phase shift of the optical signal contains information on the nature of the charge transfer and adsorption process [11, 12].

Recently, it has been reported that some amphoteric rhodamine derivatives are spontaneously adsorbed at the nonpolarized liquid/liquid interface [13, 14], and they have been studied as fluorescence probes for estimating the interfacial structure [15, 16]. The excitation energy transfer dynamics of rhodamines at the interface were investigated by means of time-resolved total internal reflection (TIR) fluorometry, and the interfacial roughness was estimated experimentally by Ishizaka et al [17–19]. In contrast, the interfacial behavior of the amphoteric rhodamine at the polarized liquid/liquid interface has rarely been studied previously. The simple transfer reaction was studied using cyclic voltammetry [20, 21], and the transient adsorption in the transfer process was studied using the AC voltammetric technique [22].

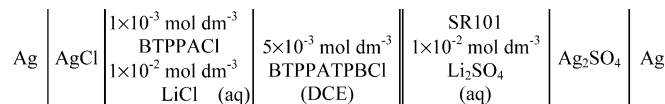
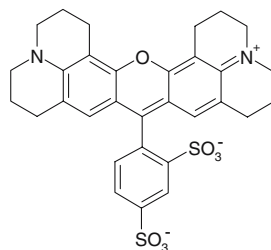
In the present work, the ion transfer of amphoteric rhodamine, sulforhodamine 101 (SR101), across the polarized water/1,2-dichloroethane interface was investigated using spectroelectrochemical techniques. The adsorption of SR101 compounds was observed in a potential region more negative than that of the transfer of the SR101 anion, and an interfacial mechanism involving the dimerization is discussed.

## Experimental

### Reagents

Sulforhodamine 101 (SR101) was purchased from Acros Organics (99% laser grade) and used after the recrystallization. The molecular structure of SR101 is displayed in Fig. 1. The electrolytes for the aqueous and the organic phases were  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$  lithium sulfate and  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$  bis(triphenylphosphoranylidene) ammonium terakis(4-chlorophenyl)borate (BTPPATPCIB), respectively. The aqueous solutions were prepared with water purified by a Milli-Q system (Millipore Milli-Q Jr.),

**Fig. 1** The molecular structure of sulforhodamine 101 (SR101)



**Fig. 2** The composition of the electrochemical cell

and 1,2-dichloroethane (DCE) as an organic solvent was used as received (Wako Chemicals 99.7% for HPLC). In the present condition, SR101 is dissolved in monoanion form in the aqueous phase. The composition of the electrochemical cell for all the measurements is represented in Fig. 2.

### Apparatus

The spectroelectrochemical cell used in all of the measurements was analogous to one reported previously [8]. The polarizable water/DCE interface had a geometrical area of 0.50 or 0.22 cm<sup>2</sup>. Platinum wires were used as counter electrodes in the water and DCE phases. Luggin capillaries were provided for the reference electrodes (Ag/Ag<sub>2</sub>SO<sub>4</sub>). Cyclic voltammograms were measured by a four-electrode potentiostat (Hokuto Denko HA1010 mM1A). The Galvani potential difference ( $\Delta_O^W \phi$ ) was estimated by taking the formal transfer potential of tetramethylammonium as 0.160 V [23].

In the differential cyclic voltfluorometry [24], the output of a metal halide lamp (Sigma Koki IMH-250) was passed through an interference filter of 550 nm (Sigma Koki VPF-25C-10-50-55000, FWHM 10.0 nm) and focused at the water/DCE interface through the organic phase. The incident angle of the light beam was fixed at 80° with respect to interface normal, providing a total internal reflection (TIR) (critical angle=67°). The counter and reference electrodes were not located on the optical path in order to avoid any photoreaction on the electrode surface. The fluorescent intensity at the emission maximum wavelength (603.5 nm) was detected by a spectrofluorometer (Jasco FP-777) or multichannel photodetector (Hamamatsu Photonics PMA11 C7473-36). The differential fluorescence intensity ( $dF/dt$ ) in TIR is described as a linear function of the faradaic current ( $I^f$ ) [24, 25],

$$\frac{dF}{dt} = \frac{4.606\varepsilon\Phi I_{ex}}{zFS \cos \psi} I^f \quad (1)$$

where  $\varepsilon$  is the molar absorptivity,  $\Phi$  is the fluorescence quantum yield,  $I_{ex}$  is the excitation photon flux,  $z$  is the charge number of transferring ion,  $F$  is the Faraday constant,  $S$  is the illuminated interfacial area, and  $\psi$  is the angle of incidence of the excitation beam.

### Potential-modulated fluorescence (PMF) spectroscopy

A combination of the four-electrode potentiostat and a digital lock-in amplifier (NF LI 5640) was employed for the PMF measurements [12]. The amplitude of potential

modulation was 10 mV with a sweep rate of  $5 \text{ mV s}^{-1}$  for the potential dependence measurement and 30 mV for the frequency response analysis at a frequency range between 0.1 and 100 Hz. A cw DPSS Nd:YAG laser (Melles Griot 58GCS405, 5 mW at 532 nm) was used as an excitation light source in the TIR condition. The AC fluorescence signal emitted from the interfacial region was measured at 616 nm, the emission maximum for the excitation at 532 nm, using a photomultiplier tube connected to a monochromator (Shimadzu SPG-120S).

## Results and discussion

### Electrochemical and spectroscopic responses in the quasi-steady-state condition

Cyclic voltammograms of SR101 at the water/DCE interface are displayed in Fig. 3. Two voltammetric responses were observed centered at  $-0.18$  and ca.  $-0.34$  V in the presence of  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  SR101. The former response exhibited a peak-to-peak separation of ca. 60 mV suggesting that the response at  $-0.18$  V is associated with the transfer process of the monoanion form of SR101 across the liquid/liquid interface, and it disappears for concentrations lower than  $1.0 \times 10^{-6} \text{ mol dm}^{-3}$  SR101 (Fig. 3b). In contrast, a narrow peak-to-peak separation,  $\sim 10$  mV, was measured at  $-0.34$  V. In order to investigate the origin of the voltammetric signals, the dependence of the differential fluorescence intensity ( $dF/dt$ ) on  $\Delta_{\text{O}}^{\text{W}}\phi$  was recorded at the emission wavelength of 603.5 nm. In the differential cyclic voltfluorometry, the potential-dependent phenomena associated with a fluorescent species could be detected without convoluting the nonfluorescent processes, such as the transfer of the electrolytes, and the differential fluorescence intensity was linearly proportional to the faradaic current [cf Eq. (1)]. As displayed in Fig. 4, the differential cyclic voltfluorogram exhibited roughly identical features to the cyclic voltammograms, in which the fluorescence responses appeared at ca.  $-0.18$  and  $-0.33$  V. The response at the negative potential was observed more clearly than with the cyclic voltammogram since the electrolyte transfer at the edge of the potential window did not affect the fluorescence response (cf Fig. 3). The peak current and the differential fluorescence intensity at  $-0.18$  V were proportional to the square root of the potential sweep rate, indicating that the transfer process was controlled by the planar diffusion of SR101 to the interface [26]. A diffusion coefficient for SR101<sup>-</sup> in the aqueous phase could be estimated as  $4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . The differential fluorescence intensities at  $-0.33$  V for SR101 exhibited a linear proportionality with the sweep rate. Assuming the voltammetric response at  $-0.33$  V was associated with the adsorption of SR101<sup>-</sup>, the peak current density ( $j_p$ ) corresponding to the adsorption phenomena can be

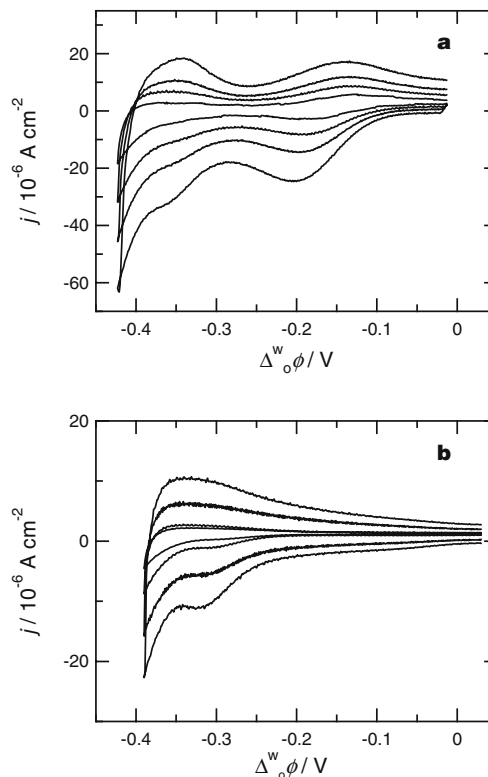
expressed by transforming the expression for solid electrodes [26],

$$j_p = \frac{z^2 F^2}{4RT} \nu \Gamma \quad (2)$$

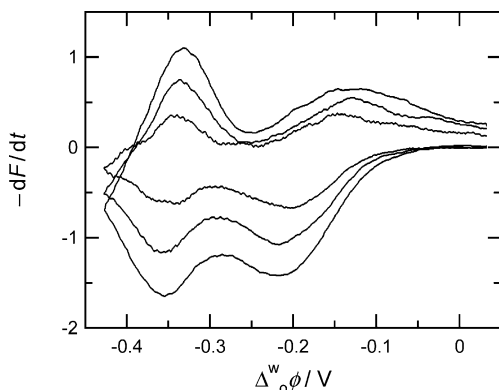
where  $\Gamma$  is the surface excess,  $\nu$  is the potential sweep rate. The value of  $\Gamma$  roughly estimated from CVs with Eq. (2) is the same order of magnitude at concentrations of SR101 higher than  $10^{-6} \text{ mol dm}^{-3}$ , and the surface excess was determined to be  $\sim 6 \times 10^{-11} \text{ mol cm}^{-2}$  (ca.  $2.8 \text{ nm}^2 \text{ molecule}^{-1}$ ) at  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ , which is close to the saturated surface concentration of amphoteric rhodamines reported in the toluene/water system [13]. In the present system, it is noteworthy that the peak potential was much more negative than the formal transfer potential; the origin of these responses is also discussed in following section.

### Dynamic spectroelectrochemical analysis

The transfer reaction of SR101 was also studied using PMF spectroscopy. The real ( $\Delta F_{\text{re}}$ ) and imaginary ( $\Delta F_{\text{im}}$ ) components of the PMF signal at various frequencies are displayed in Fig. 5. The most prominent signal was found around  $-0.32$  V, which decreased as the frequency of potential modulation increased. A weak response was also observed around the transfer potential in the presence of

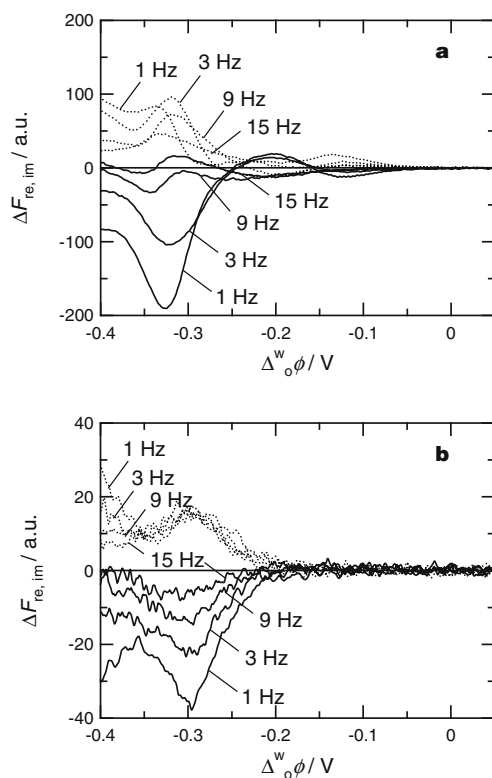


**Fig. 3a, b** Cyclic voltammograms for SR101 at 20, 50, 100, and 200  $\text{mV s}^{-1}$ . The concentrations of SR101 in the aqueous phase were **a**  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  and **b**  $1.0 \times 10^{-6} \text{ mol dm}^{-3}$ .



**Fig. 4** Differential cyclic voltfluorograms measured in the presence of  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$  SR101 at 20, 40, and 60  $\text{mV s}^{-1}$ . The excitation and detected emission wavelengths were 550 and 603.5 nm, respectively

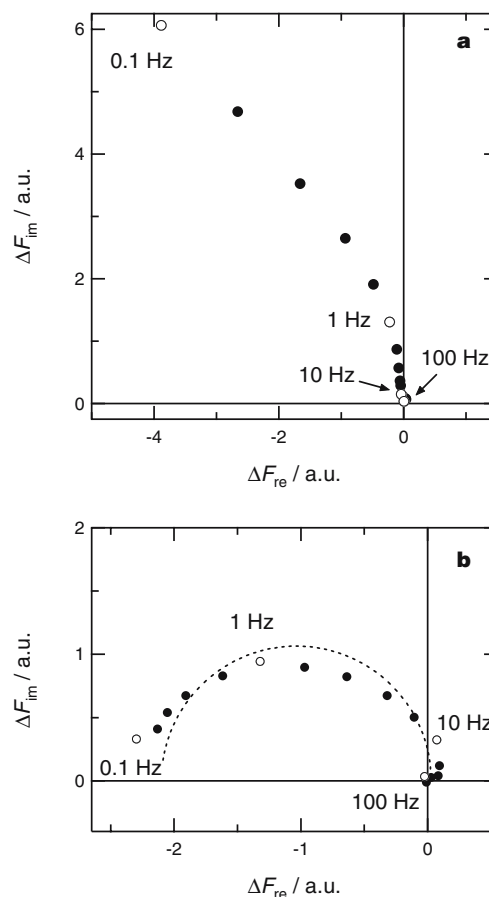
$1 \times 10^{-4} \text{ mol dm}^{-3}$  SR101 (Fig. 5a). The negative real and positive imaginary components at potentials lower than  $-0.15 \text{ V}$  were associated with the transfer of anionic species, i.e., the SR101 anion. In addition, the measurable PMF signal in the range of  $-0.15$  to  $-0.25 \text{ V}$ , clearly seen at low frequencies, suggests that complex adsorption phenomena are involved in the ion transfer process across the liquid/liquid interface. The PMF response at the transfer



**Fig. 5** Dependences of the PMF response on the Galvani potential difference in the presence of **a**  $1 \times 10^{-4} \text{ mol dm}^{-3}$  and **b**  $1 \times 10^{-6} \text{ mol dm}^{-3}$  SR101 in the aqueous phase. The *solid* and *dashed* lines denote the real and imaginary components of PMF signals, respectively. The excitation and detected emission wavelengths were 532 nm and 616 nm, respectively. The amplitude of potential modulation was 10 mV with a sweep rate of  $5 \text{ mV s}^{-1}$

potential was significantly decreased when the bulk concentration of SR101 was lowered (Fig. 5b).

The dynamic PMF responses at  $-0.13 \text{ V}$  were measured in the presence of  $1 \times 10^{-4} \text{ mol dm}^{-3}$  SR101 by analyzing the frequency dependence of the PMF signal in the range 0.1–100 Hz (Fig. 6a). The magnitude of the PMF signals basically increased lower frequencies of potential modulation, and the non-linear relation between the negative real and positive imaginary components confirmed the presence of the transient adsorption process in the ion transfer of SR101 anions across the interface. In a water/nitrobenzene system, the ion transfer of analogous amphoteric rhodamine dye, sulforhodamine B (SRB), has been reported to be coupled with the transient adsorption at the ion transfer potential [22]. These results suggest that the affinity of the dyes to the interfacial region was introduced by a strong local hydrophilicity associated with the sulfonate groups. The transfer mechanism of SR101 around  $-0.18 \text{ V}$  is similar to that of SRB. On the other hand, the response of SRB corresponding to that of SR101 at  $-0.32 \text{ V}$  has not been mentioned because the potential window would be limited by the transfer of an organic supporting electrolyte.



**Fig. 6** Complex representation of PMF response at **a**  $-0.13 \text{ V}$  and **b**  $-0.31 \text{ V}$ . The potential modulation was 30 mV. The initial concentrations of SR101 were **a**  $1 \times 10^{-4} \text{ mol dm}^{-3}$  and **b**  $1 \times 10^{-6} \text{ mol dm}^{-3}$  SR101 in the aqueous phase. The *dashed* line is the theoretical curve for the adsorption process of dianion by Eq. (3)



The frequency response measurement of PMF signals at  $-0.31$  V was also carried out in the presence of  $1 \times 10^{-6}$  mol  $\text{dm}^{-3}$  SR101 to avoid overlapping with the PMF responses for the transfer from  $-0.15$  to  $-0.25$  V (cf Fig. 5). As shown in Fig. 6b, the complex plane of PMF is represented as a semicircle, in which the real component approached zero at the high frequency limit, and the imaginary component reached the maximum around 1.5 Hz. These features are typically obtained for the kinetically controlled adsorption process [11]. The PMF responses associated with the adsorption processes from the aqueous phase and from the organic phase showed a distinctive phase shift originating from the opposite dependence of the adsorption/desorption kinetics on the Galvani potential difference. On the basis of our previous analysis, the PMF responses around  $-0.32$  V, in which the real and imaginary components appeared as negative and positive signs, are consistent with the adsorption process of anionic species from the aqueous phase or of cationic species from the organic phase. As described above, the spectroelectrochemical data apparently indicate that the transfer of  $\text{SR101}^-$  from the aqueous phase to the organic phase takes place at  $-0.18$  V, and the adsorption processes of the anionic monomer are unfavorable in the aqueous phase at more negative potentials such as  $-0.32$  V. As the cationic fluorescent species is not included in the organic phase, the results suggest the presence of additional interfacial processes such as the dimer formation, although no substantial spectroscopic

changes in the absorption and emission spectra were observed in the bulk phases in the concentration range below  $1 \times 10^{-4}$  mol  $\text{dm}^{-3}$ . Frequently, the xanthene dye forms a dimer in the solution [27–29]. In cases in which the monomer is preferentially adsorbed at the interface, the number density of monomers in the interfacial region is much higher than in the bulk solution, and the dimerization would occur more easily at the interface. The molecular association of ionic dyes at the liquid/liquid interface has been observed without formation of the associate in the bulk phase using surface-sensitive nonlinear spectroscopy [6, 14, 30]. Therefore, the spectroelectrochemical responses around  $-0.32$  V possibly correspond to the formation and adsorption of the anionic dimer  $\left(\text{SR101}\right)_2^{2-}$  even though the dimer formation was not observed in the bulk phase. At the present neutral pH conditions, SR101 was initially located in the aqueous phase as a monoanionic form,  $\text{SR101}^-$ , including two anionic sulfo groups and a positive charge (cf the molecular structure in Fig. 1). The dimer formation will be caused by a  $\pi$ - $\pi$  interaction of xanthene moieties and an electrostatic interaction between the sulfo group and the positive charge [28, 29]. The PMF response for the simple adsorption process in the aqueous phase ( $\Delta F_a$ ) can be expressed by the surface coverage ( $\theta_0$ ) and the adsorption ( $k_{a,0}$ ) and desorption rate constants ( $k_{d,0}$ ) [11],

$$\Delta F_a = \frac{2.303\varepsilon\Phi I_{\text{ex}}\Gamma_s SbzF}{RT} \left[ \frac{\Delta_O^W \phi_1 (k_{a,0}c_0\alpha(1-\theta_0) - k_{d,0}(\alpha-1)\theta_0)}{k_{a,0}c_0 + k_{d,0} + i\omega} \right] \quad (3)$$

where  $\Gamma_s$  is the saturated surface concentration,  $b$  is the portion of the applied potential developed in the aqueous side of the interface,  $\alpha$  is overall transfer coefficient for adsorption process, and  $c_0$  is the bulk concentration.  $\Delta_O^W \phi_1$  and  $\omega$  are the amplitude and the angular frequency of AC potential modulation. The experimental data fit in with the theoretical curve for the adsorption of dianion (dashed line in Fig. 6b). In the present SR101 system, however, the kinetic parameters such as the adsorption/desorption rate constants could not be estimated with unknown parameters including the interfacial dimerization constant at a given potential. The PMF response around  $-0.32$  V could also involve the fluorescence response from the monomer species produced by dissociation of the dimer during the adsorption/desorption processes. Further study to elucidate the detail of the interfacial behavior of amphoteric rhodamine dyes with different molecular structures is ongoing.

## Conclusions

The ion transfer of amphoteric rhodamine, SR101, at the polarized water/1,2-dichloroethane interface was studied

using spectroelectrochemical techniques. Two characteristic voltammetric responses were found at  $-0.18$  and  $-0.32$  V. The PMF complex plane indicated the presence of the transient adsorption process in the ion transfer of SR101 monoanion at  $-0.18$  V. The semicircle PMF complex plane was also obtained at  $-0.3$  V, and it was demonstrated that the adsorption of the dianionic dimer took place at more negative potentials than the transfer of the monoanion. These results provide relevant information for the use of this dye as a fluorescence probe in lipid bilayers as well as self-organized microheterogeneous systems. For instance, assuming that the membrane potential is negative enough to transfer the dye into the organic medium, a substantial contribution of the fluorescence signal will arise from dyes specifically adsorbed at the boundary. Although extrapolation of the physical properties of liquid/liquid interface to lipid bilayers should be done cautiously, clear evidence for the adsorption of amphoteric dyes in the transfer reaction across the interface was demonstrated by the spectroelectrochemical techniques. The experimental approaches highlighted in this report may offer valuable information on the interfacial behavior of fluorescence probes at the boundary between two dielectric media.

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