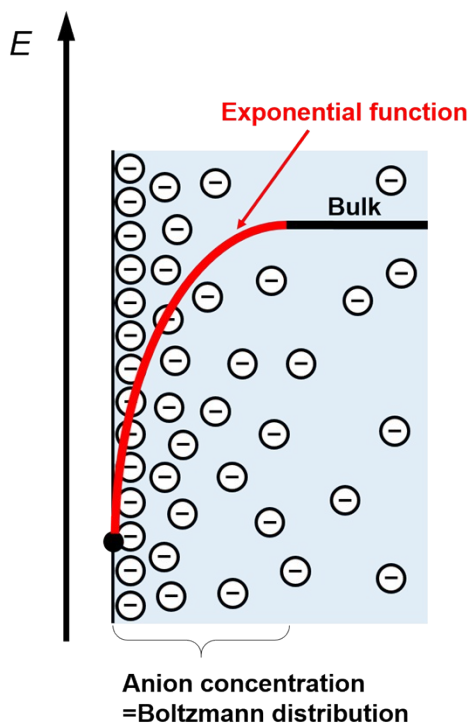# Supporting Information

Chemical Potentials of Electric Double Layers at Metal-Electrolyte Interfaces: Dependence on Electrolyte Concentration and Electrode Materials, and Application to Field-Effect Transistors

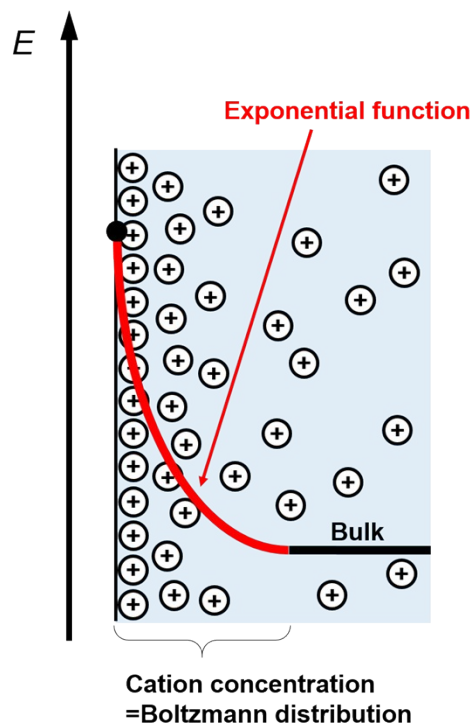Chihiro Nanjo,[a] Daisuke Yokogawa,[b] Michio M. Matsushita[a] and Kunio Awaga*[a]

[a]Department of Chemistry & Integrated Research Consortium on Chemical Sciences (IRCCS), Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

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(a)

(b)

E

E

Exponential function

Exponential function

Bulk

Bulk

**Anion concentration
=Boltzmann distribution**

**Cation concentration
=Boltzmann distribution**

Scheme S1 The Gouy-Chapman model: the concentration distribution of ions follows the Boltzmann distribution, and the potential follows the exponential function. Panels (a) and (b) show the cases of anions and cations, respectively.

Conversion of V_{MR} to E_M

The potential energies of metal electrodes E_M were obtained, using the following equation:

$$E_M = -eV_{MR} + E_R,$$ (S1)

which was from eq. (1). Since the potential energy of SHE was reported as −4.44 eV,[1] and that of

the present Ag/AgCl reference electrode was −0.195 eV (*vs.* SHE at 298 K), E_R of this reference

electrode was calculated as −4.64 eV.

Derivation of eq. (7)

Using the Gouy-Chapman model, the relation between the surface charge q and the electric potential ψ on the surface of metal electrode is expressed as

$$q = sgn(\psi)\sqrt{\epsilon_0\epsilon_s k_B T(z^+ - z^-)c_0}\sqrt{2\left(\frac{z^+\exp\left(\frac{-z^- F\psi}{RT}\right) - z^-\exp\left(\frac{-z^+ F\psi}{RT}\right)}{z^+ - z^-} - 1\right)},\tag{S2}$$

where ϵ_0 and ϵ_s are the electrical permittivity of vacuum and the dielectric constant of the solution without the electrolyte, respectively, k_B is the Boltzmann constant, z^+ and z^- are the valences of the cation and anion, respectively, and c_0 is the bulk concentration of the salt.[65] The bulk concentrations of the cation and anion are expressed as $-z^- c_0$ and $z^+ c_0$, respectively. The dimensionless surface charge density in EDL is defined as

$$\sigma_D = -sgn(\psi)\sqrt{\frac{z^+ - z^-}{2z^+(-z^-)}}\sqrt{2\left(\frac{z^+\exp\left(\frac{-z^- F\psi}{RT}\right) - z^-\exp\left(\frac{-z^+ F\psi}{RT}\right)}{z^+ - z^-}\right)},\tag{S3}$$

by dividing the left and right of eq. (S2) by $\sqrt{\epsilon_0\epsilon_s k_B T z^+(-z^-)c_0}$.

Equation (S3) is approximated as

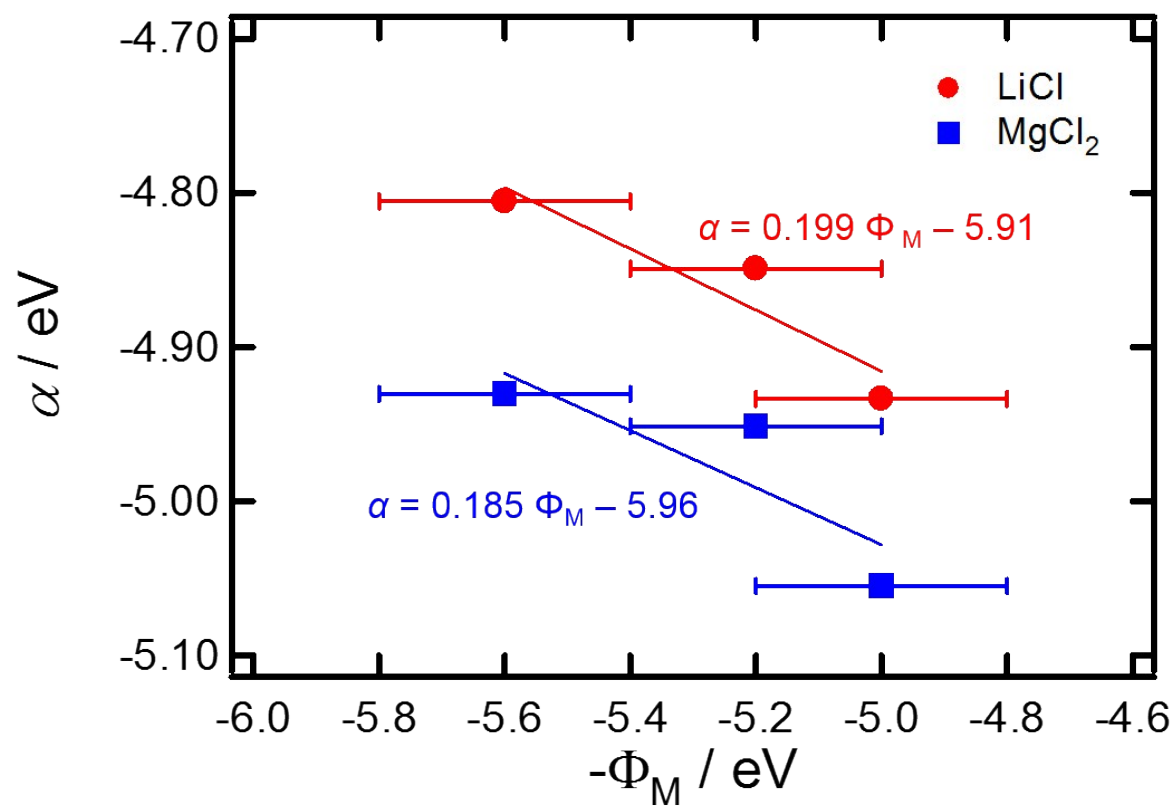$$\sigma_D \sim \begin{cases} -\sqrt{\dfrac{1}{-z^-}}exp\left(\dfrac{-z^- F\psi}{2RT}\right) & \psi \gg 0 \\[4mm] \sqrt{\dfrac{1}{z^+}}exp\left(\dfrac{-z^+ F\psi}{2RT}\right) & \psi \ll 0 \end{cases}.\tag{S4}$$

Equation (S4) is rewritten as

$$\psi \sim \begin{cases} -\dfrac{2RT}{z^-F}\ln\!\left(-\sqrt{-z^-}\,\sigma_D\right) & \sigma_D \ll 0 \\[2ex] -\dfrac{2RT}{z^+F}\,\ln\!\left(\sqrt{z^+}\,\sigma_D\right) & \sigma_D \gg 0 \end{cases}$$

(S5)

Using the charge of the ionic species z ($z = z^+$ or z^-), eq. (7) is derived as

$$\psi \sim -\frac{2RT}{zF}\ln\!\left(\sqrt{|z|}\,|\sigma_D|\right)$$

(7)

Figure S1 Work function dependence of the fitting parameter α in Table 1 for the PEG solutions of LiCl and $MgCl_2$.

Relation between ln κ and Φ_M

As shown in Fig. S1, the values of α are approximately proportional to Φ_M, and, as shown in eq. (10), α is also proportional to ln κ. Therefore, we can expect a linear relation between Φ_M and ln κ, namely

$$ln\ \kappa \propto - \Phi_M .$$ (S6)

Since the proportionality coefficients between α and Φ_M for the LiCl and $MgCl_2$ solutions in Fig. S1, are nearly the same, the proportionality coefficients between Φ_M and ln κ would depend little on the electrolytes.
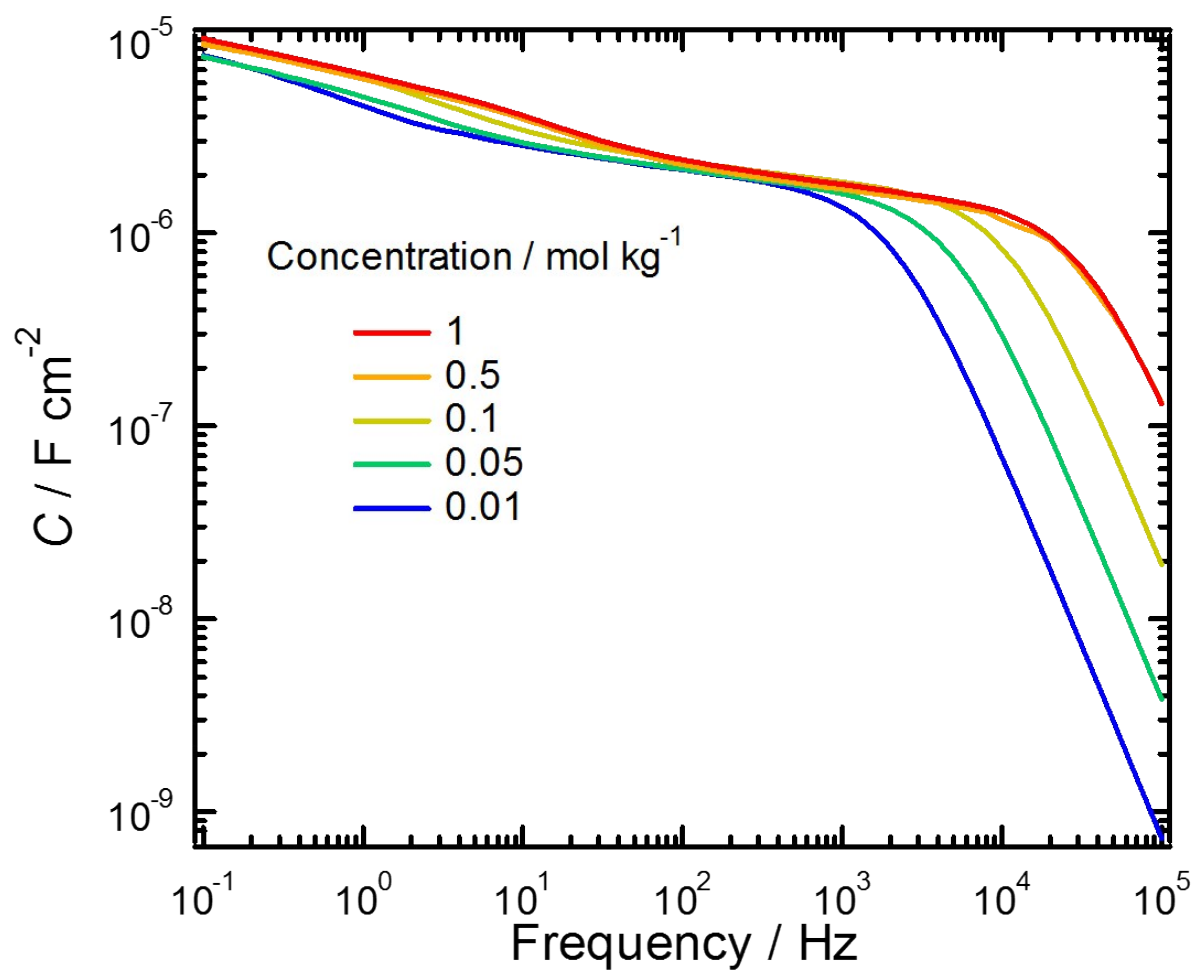
Figure S2 Frequency dependence of the capacitance for the LiCl-PEG solutions.

Table S1 Concentration dependence of the capacitance at 0.1 Hz for the LiCl-PEG solutions, and the FET parameters for the PtPc EDL-FETs of the LiCl-PEG solutions.

Concentration / mol kg^{-1}	Capacitance C / F cm^{-2}	Mobility μ / cm^2 V^{-1} s^{-1}	Threshold voltage V_T / V	on/off ratio
0.01	8.3×10^{-6}	1.2×10^{-3}	-0.8	1.4×10^3
0.05	8.2×10^{-6}	2.5×10^{-3}	-0.74	2.8×10^3
0.1	9.6×10^{-6}	2.0×10^{-3}	-0.66	3.0×10^3
0.5	9.5×10^{-6}	2.7×10^{-3}	-0.65	5.2×10^3
1	1.0×10^{-5}	2.5×10^{-3}	-0.62	3.4×10^3

Calculations for mobilities, threshold voltages and on/off ratios

The transistor performances shown in Table S1 was calculated by the following procedure. The mobilities μ were calculated by the equation $\mu = (\partial I_D / \partial V_G) (L / wCV_D)$, where L, w, C were channel length (1.0×10^{-3} cm), channel width (20 cm), and capacitance of the gate-dielectrics. The values of $\partial I_D / \partial V_G$ were obtained from the slope of the linear region of the transfer characteristics. The threshold voltages V_T were obtained from the $|Id|^{1/2}$ *vs.* V_G plots. The on/off ratios were obtained from the ratio of the maximum and minimum values of I_D in the transfer characteristics.
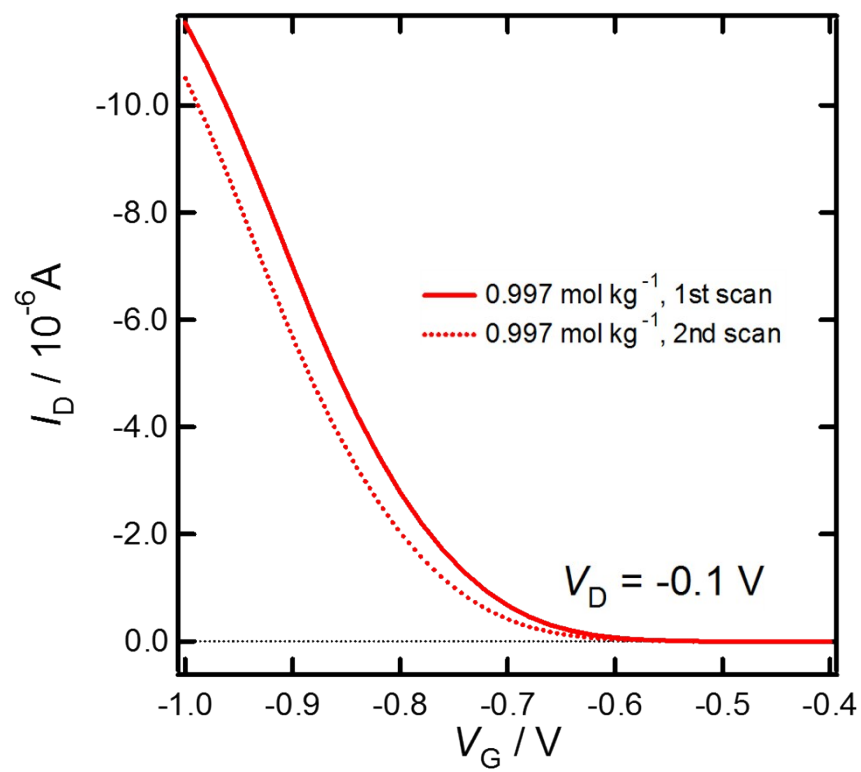
Figure S3 Comparison between the 1st and 2nd scans for the transfer characteristics of the PtPc

EDL-FET with the LiCl-PEG solutions of 0.997 mol kg^{-1}.

References

1 S. Trasatti, *Pure & Appl Chem.*, 1986, **58**, 955.