

SUPPORTING INFORMATION

Supporting Electrolyte and Solvent Effects On Single Electron Double Layer Capacitance Charging of Hexanethiolate-Coated Au₁₄₀ Nanoparticles

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e/ΔV is a differential not an integral capacitance.

A key premise of this paper is that over the region of interest, essentially the potential spacings between the peaks of interest, we can write:

$$\frac{\Delta V}{\Delta q} \cong \frac{1}{C_d} \quad \text{S-1}$$

where C_d is the differential capacitance, ΔV is a finite change in potential and Δq is a finite change in charge. For the charging of a mono-disperse collection of MPCs, Chen et al (Ref. 8a) showed that the standard potential, $E_{z+1/z}^0$, obtains when the number of MPCs with charge n_{z+1} equals the number with charge n_z ; similarly, the standard potential, $E_{z/z-1}^0$, obtains when the number of MPCs with charge n_z equals the number with charge n_{z-1} .

The difference in these two standard potentials, $E_{z+1/z, c_{SE}}^0 - E_{z/z-1, c_{SE}}^0$ defines the change in potential required to convert the system from the condition where $n_{z+1} = n_z$ to the condition where $n_z = n_{z-1}$ - a transition that requires the transfer of a single unit of charge per MPC if we assume that virtually all of the charge resides essentially in two forms at the standard potential. Thus Equation S-1 can be expressed as:

$$E_{z+1/z, c_{SE}}^0 - E_{z/z-1, c_{SE}}^0 \cong \frac{e}{C_{\text{MPC}, z}} \quad \text{S-2}$$

where $C_{\text{MPC}, z}$ is differential capacitance approximately at the point where the MPC has z charges. This equation is valid for a given value of the concentration of supporting

electrolyte, c_{SE} . We can express $C_{\text{MPC},z}$ in terms of its compact and diffuse differential capacitive components:

$$\frac{1}{C_{\text{MPC},z}} = \frac{1}{C_{\text{COMPACT},z}} + \frac{1}{C_{\text{DIFFUSE},z,c_{\text{SE}}}} \quad \text{S-3}$$

Combining Equations S-1 and S-2 gives

$$E_{z+1/z,c_{\text{SE}}}^0 - E_{z/z-1,c_{\text{SE}}}^0 \cong \frac{e}{C_{\text{MPC},z}} = e \left(\frac{1}{C_{\text{COMPACT},z}} + \frac{1}{C_{\text{DIFFUSE},z,c_{\text{SE}}}} \right) \quad \text{S-4}$$

We assume that only $C_{\text{DIFFUSE},z,c_{\text{SE}}}$ is a function of c_{SE} . The value of $E_{z+1/z,c_{\text{SE}}}^0 - E_{z/z-1,c_{\text{SE}}}^0$ is experimentally determined and the values of $C_{\text{DIFFUSE},z,c_{\text{SE}}}$ can be theoretically computed using the spherical diffuse layer simulation. A plot of $E_{z+1/z,c_{\text{SE}}}^0 - E_{z/z-1,c_{\text{SE}}}^0$ vs $e/C_{\text{DIFFUSE},z,c_{\text{SE}}}$ for a given z and different values of c_{SE} should have a slope of unity and an intercept of $e/C_{\text{COMPACT},z}$. A slope of unity along with a sensible intercept (likely different for different values of z) confirms the validity of the analysis, as is shown in Figure 4. The analogous plot of Gouy Chapman C_{DIFFUSE} calculations according to Equation 1, shown as Figure S-5, shows that the flat-surface model is a poor approximation for nanoparticles.

Figure Legends

Figure S-1. Cyclic voltammogram (CV) of 0.08 mM $\text{Au}_{140}(\text{SC6})_{53}$ in CH_2Cl_2 with 0.1 M Bu_4NClO_4 at 283 K.

Figure S-2. Capacitance versus MPC core charge state plot of 0.08 mM $\text{Au}_{140}(\text{SC6})_{53}$ in CH_2Cl_2 with different Bu_4NClO_4 concentrations at 283 K. At core charge states +2, +1, 0, -1, -2, -3. In taking the capacitances from OSWV data, peak potentials taken in forward and reverse potential scans are averaged in order to cancel the residual IR_{UNC} distortion of the peak position, which is important at low Bu_4NClO_4 concentrations.

Figure S-3. Osteryoung square wave voltammogram (OSWV) of 0.05 mM $\text{Au}_{140}(\text{SC6})_{53}$ in THF with Bu_4NClO_4 (0.1 M) as the supporting electrolyte at 283 K.

Figure S-4. U_{dl} versus $\log_{10}(\kappa r_0)$ plot based on numerical simulation of spherical diffuse layer. $U_{\text{dl}} = Z_{\text{SE}} e \phi_2 / k_{\text{B}} T$, $\kappa = (2n_{\text{SE}} Z_{\text{SE}}^2 e^2 / \epsilon \epsilon_0 k_{\text{B}} T)^{1/2}$, $Z_{\text{norm}} = Z_{\text{SE}} Z_{\text{MPC}} e^2 / (4\pi r_0 \epsilon \epsilon_0 k_{\text{B}} T)$, r_0 is the summation of the Au_{140} MPC core radius and the hexanethiolate monolayer thickness (i.e., $r_{\text{CORE}} + d$). Z_{SE} is the charge of the supporting electrolyte ions, which is 1 for Bu_4NClO_4 , n_{SE} is the number concentration of Bu_4NClO_4 , Z_{MPC} is the MPC core charge state, and the rest symbols have their usual meaning. $U_{\text{dl}}(\text{SIM})$ is the spherical simulation result, while $U_{\text{dl}}(\text{GC})$ is the result based on Gouy-Chapman theory (planar electrode SAM). $\log_{10}(\kappa r_0)$ falls in between -0.293 and 0.703 (see vertical lines) when Bu_4NClO_4 concentration varies from 1.02 mM to 100.3 mM at 283K. (a) $Z_{\text{NORM}} = 8.2$, when $Z_{\text{MPC}} = 2$, $Z_{\text{SE}} = 1$, $T = 283\text{K}$. (b) $Z_{\text{NORM}} = 20.5$, when $Z_{\text{MPC}} = 5$, $Z_{\text{SE}} = 1$, $T = 283\text{K}$. It is obvious that when Z_{MPC} becomes larger, $U_{\text{dl}}(\text{GC})$ is getting closer to $U_{\text{dl}}(\text{SIM})$ results.

Figure S-5. Plot of Equation 1, according to experimental C_{MPC} data and C_{DIFFUSE} calculations from Gouy-Chapman theory (Ref. 7a). Slopes are 0.45 (+2 charge state), 1.21 (+1 charge state), 0.40 (0 charge state), and 1.20 (-1 charge state).

Figure S-1.

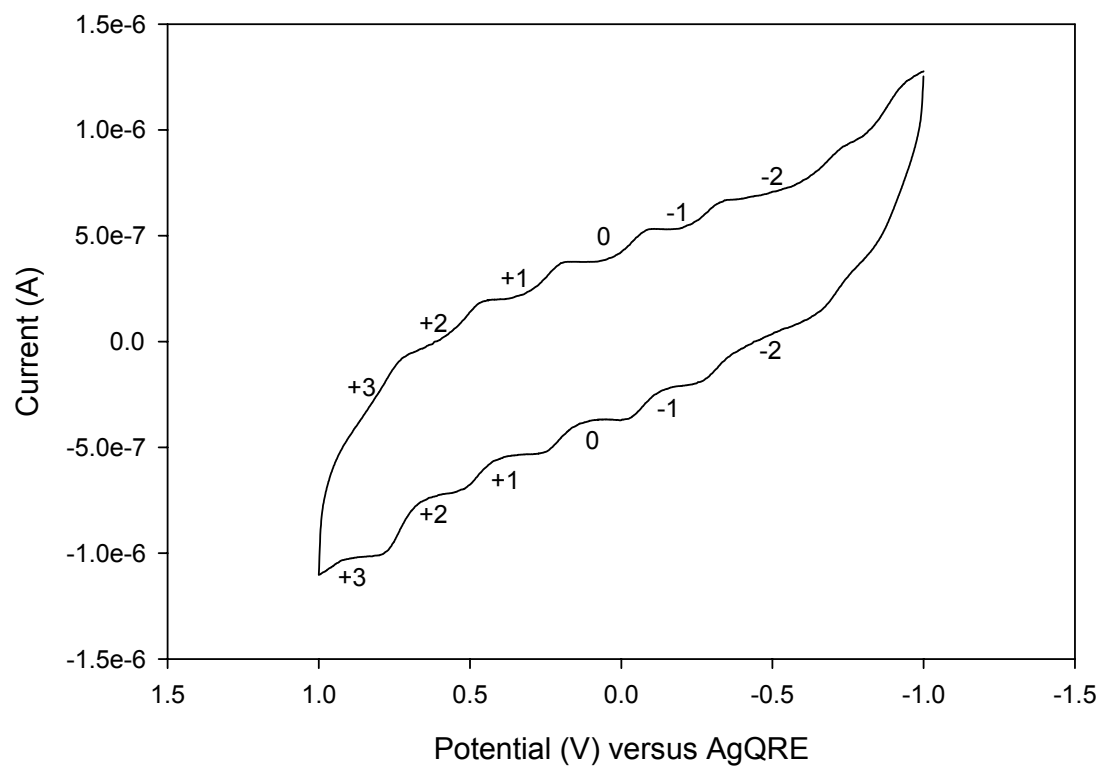


Figure S-2.

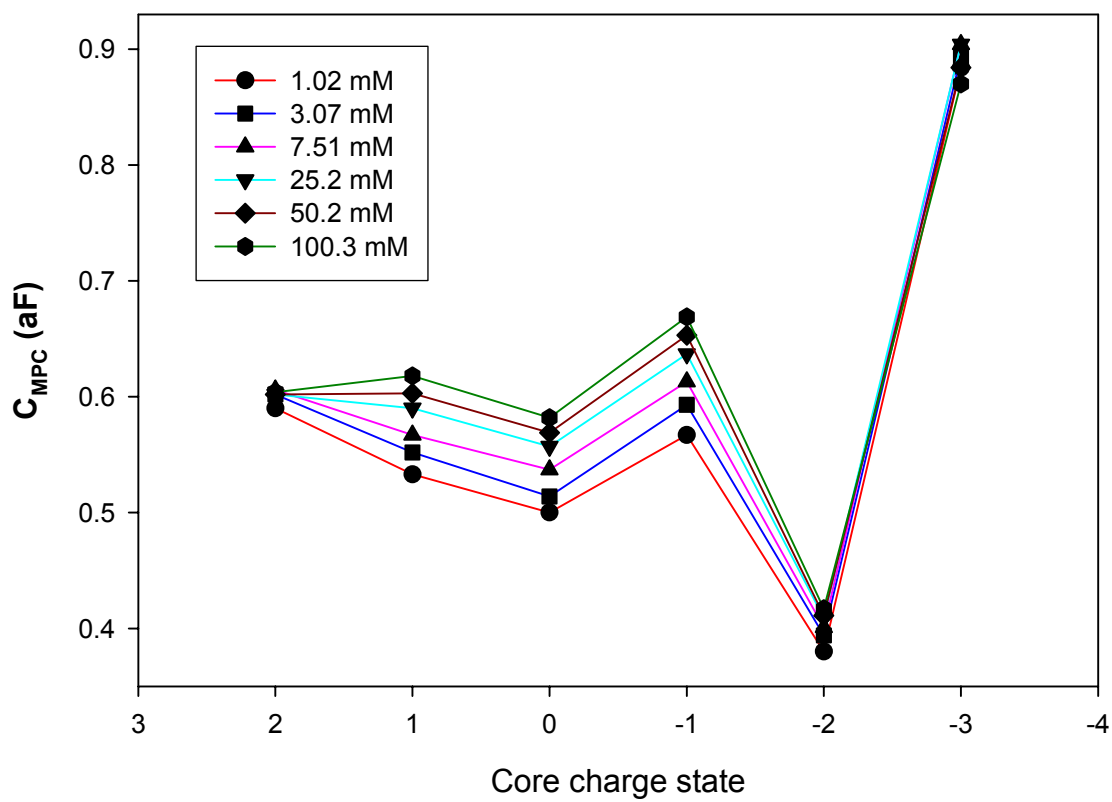


Figure S-3.

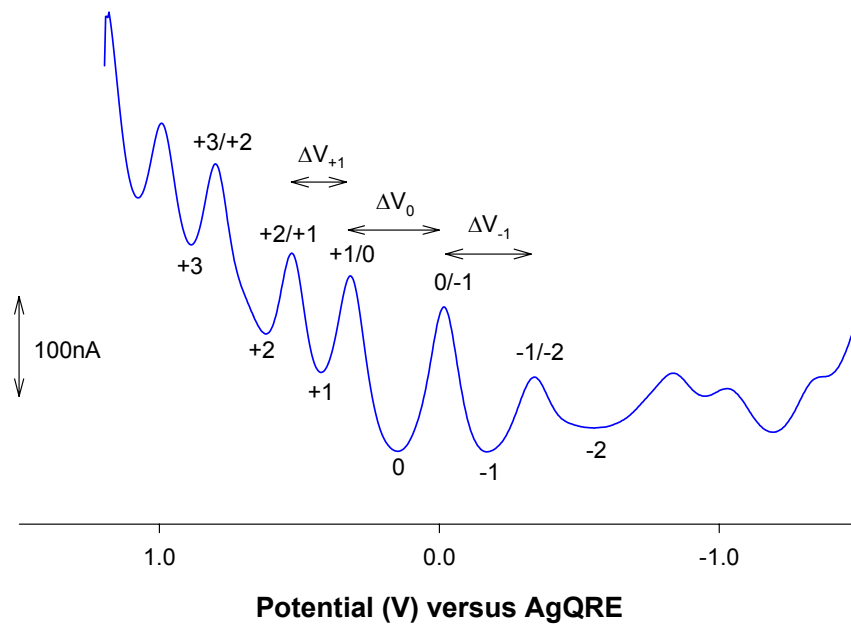


Figure S-4 (a)

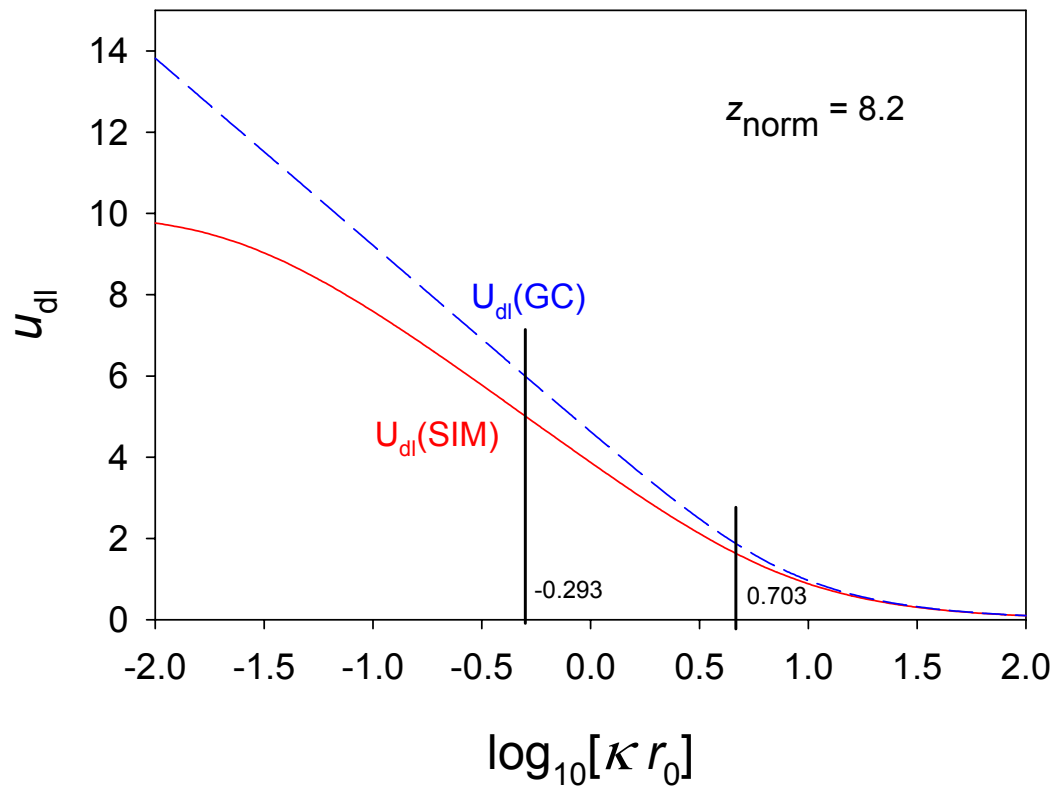


Figure S-4 (b)

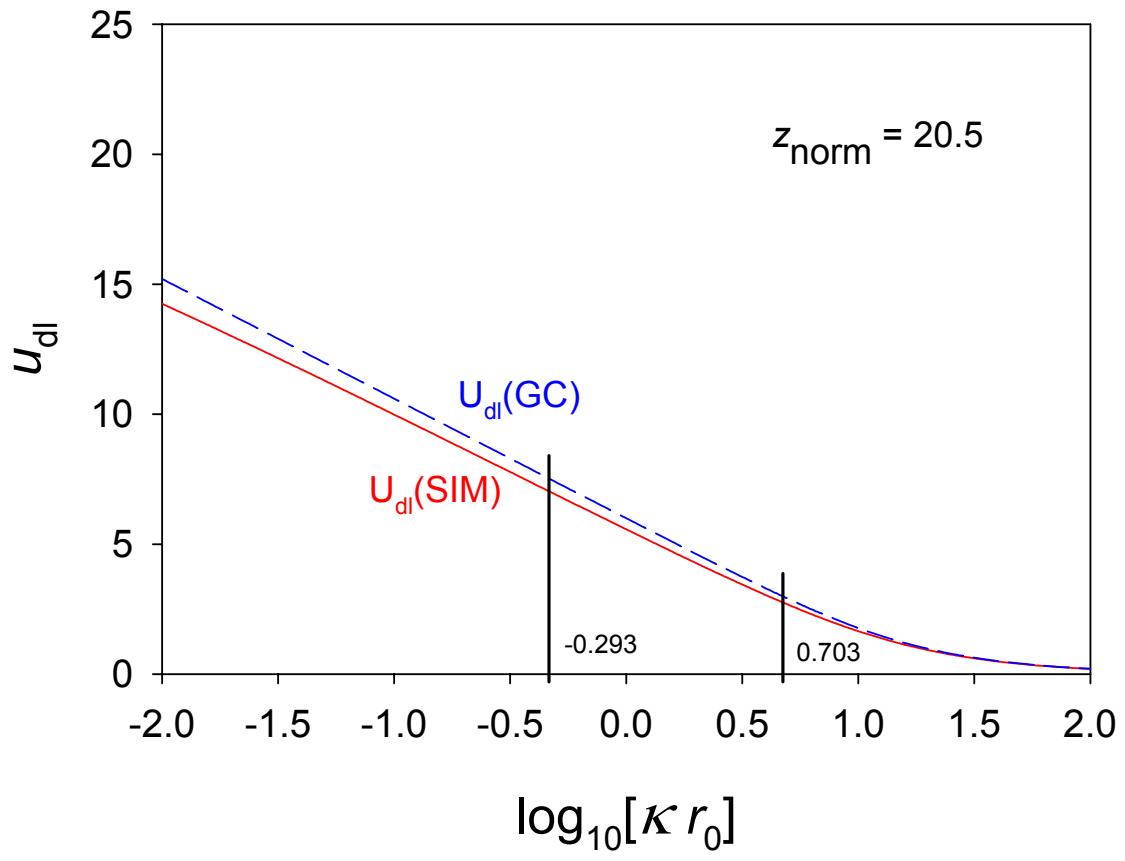


Figure S-5

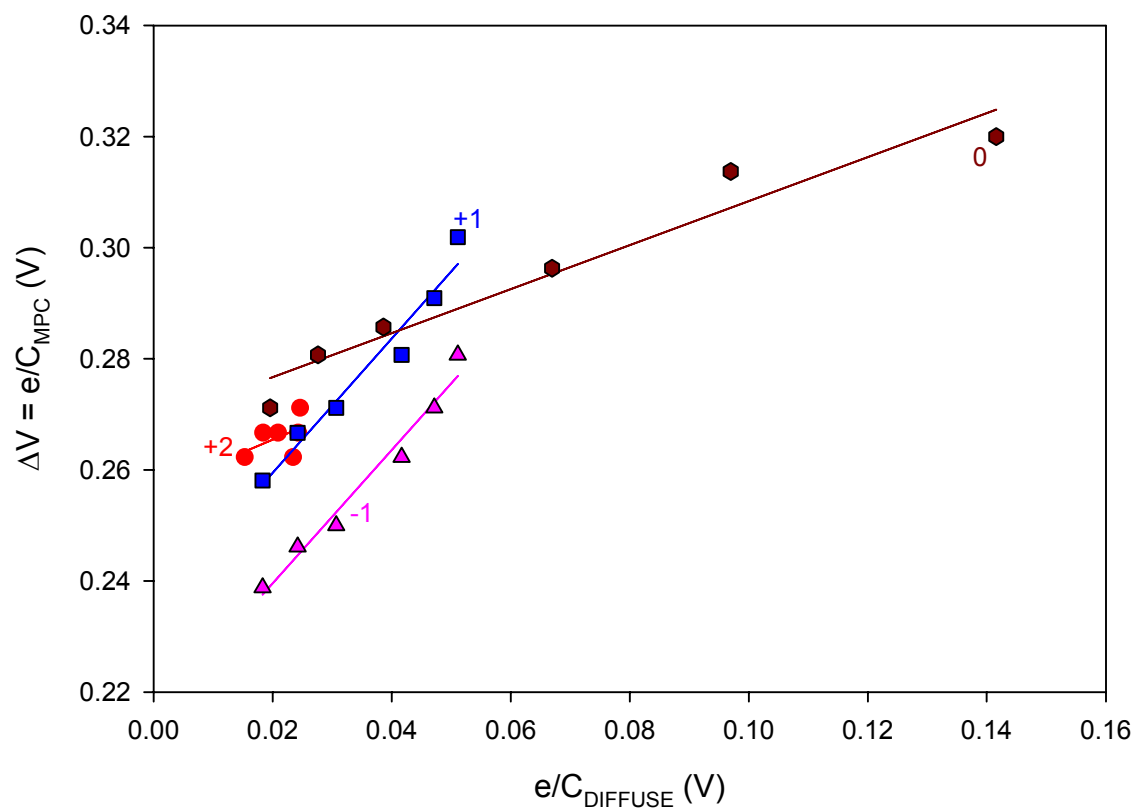


Table S-1. Capacitance of 0.08 mM Au₁₄₀(SC6)₅₃ at different core charge states in CH₂Cl₂ with different Bu₄NClO₄ concentrations at 283 K (calculated from $e/\Delta V$, where ΔV is the average peak to peak spacing of forward and reverse scans of OSWV in Fig.1). C_{MPC-2} and C_{MPC-3} are the effective capacitances.

Bu ₄ NClO ₄ (mM)	C _{MPC+2} (aF)	C _{MPC+1} (aF)	C _{MPC0} (aF)	C _{MPC-1} (aF)	C _{MPC-2} (aF)	C _{MPC-3} (aF)
1.02	0.59	0.53	0.50	0.57	0.38	0.88
3.07	0.60	0.55	0.51	0.59	0.39	0.89
7.51	0.61	0.57	0.54	0.61	0.40	0.90
25.2	0.60	0.59	0.56	0.64	0.41	0.90
50.2	0.60	0.60	0.57	0.65	0.41	0.88
100.3	0.61	0.62	0.59	0.67	0.42	0.87