Supplementary Information

"Particle Adsorption on Hydrogel Surfaces in Aqueous Media due to van der Waals Attraction"

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A. Interaction potential between charged particles and like-charged poly (acrylamide - acrylic acid) gel

We performed adsorption experiment of negatively charged polystyrene particles (a_p = 300 nm, Z = 3256) onto negatively charged poly (acrylamide - acrylic acid) [hereafter designated as P(AAm-AAc)] copolymer gel in water. P(AAm-AAc) gels were synthesized from acrylamide and acrylic acid monomers (molar ratio = 95 : 5).

The electrostatic interaction potential U_e (x) between a charged sphere and a flat surface separated by a distance x is given by

$$U_e(x) = a_p \varepsilon_m \psi_1 \psi_2 \log[1 + \exp(-\kappa x)]$$

Here, ψ_1 and ψ_2 are the electrostatic potentials on the particle and gel surfaces, respectively. The value of ψ_1 was assume to be the same as the ζ potential determined by electrophoresis (-50 mV). ψ_2 was estimated based on Donnan equilibrium between the gel and outer phase ($\psi_2 = \psi_s$ Fig.S1), given by

$$y_s + (\alpha - 1)\frac{2}{Q}\cosh y_s = ln\left[\sqrt{\left(\frac{Q}{2}\right)^2 + 1} + \frac{Q}{2}\right] - \frac{\sqrt{\left(\frac{Q}{2}\right)^2 + 1} - \alpha}{\frac{Q}{2}}$$

Here $y_s = -(e_0\psi_s)/(k_BT)$, $Q = q/n_i$, and $\alpha = (\varepsilon_o n_0)/(\varepsilon_i n_i)$ [e_0, the elementary charge; q, number density of the fixed charge in gel; n_i and n_o, ion concentrations inside and outside the gel; ε_i and ε_o, permittivity of the gel and of medium, respectively]. q value was calculated from dissociation constant of AAc monomer. The total interaction potential $U = U_e + U_{vdW}$ calculated at various values of [NaCl] (5–50 mM) is shown in Fig.S2. The potential curves had secondary minima, which became deeper on increasing [NaCl]s. The depth of the potential is 1 k_BT at x ~ 10 nm, at [NaCl] = 50 mM. Figure S3 shows the area fraction ϕ of adsorbed particles plotted against [NaCl]. The ϕ value increased on increasing [NaCl], as expected from the potential curves.

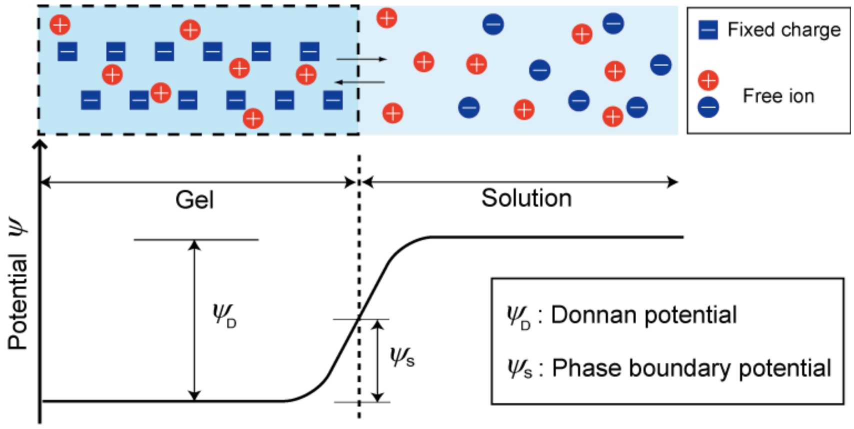

Figure S1 An illustration of Donnan potential and surface potential of charged gel.

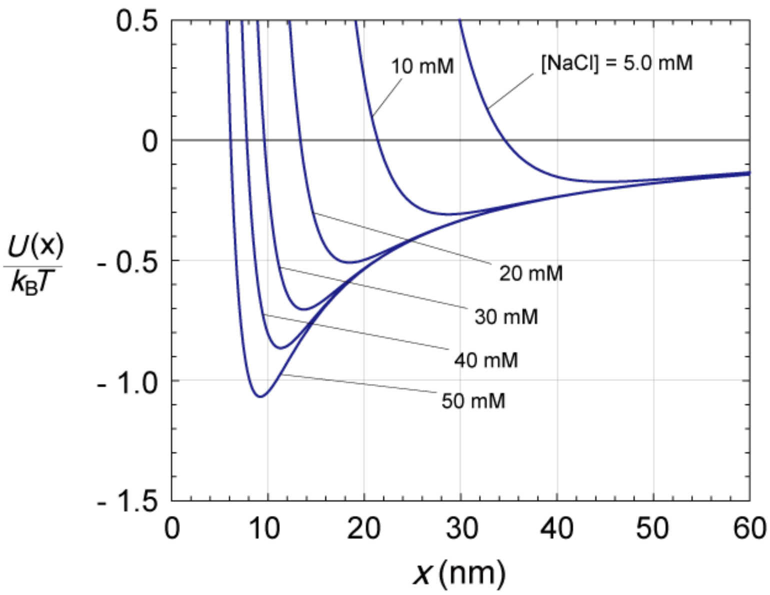

Figure S2 Influence of [NaCl] on the interaction potential $U(x)$ between the charged particle and like charged gel.

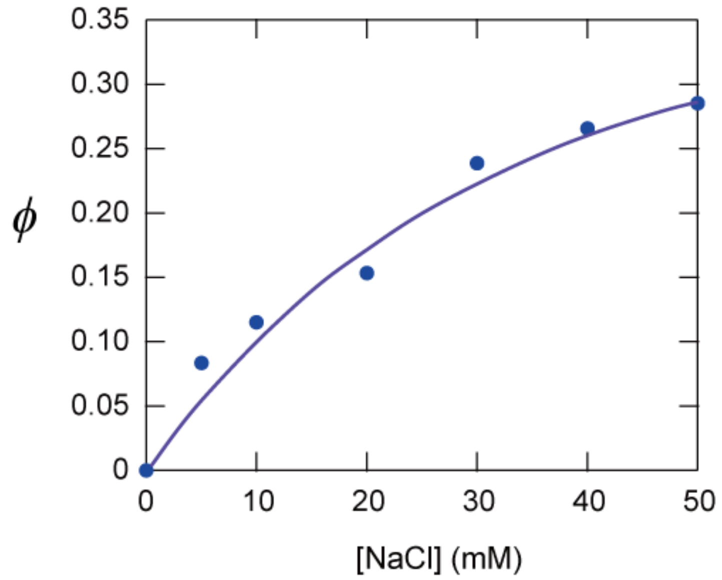

Figure S3 ϕ *vs*. [NaCl] plot for the P(AAm-AAc) gel.

B. Equilibrium sizes of PAAm-based gel and PDMA gel at various values of C_{EG}.

Figure S4 shows diameters of disk shaped PAAm-based gel [taken from reference 29] and PDMA gel in equilibrium swelling at various values of C_{EG} (reduced by the diameter in pure water, d_w). The sample size did not significantly vary on changing C_{EG} for both gel samples.

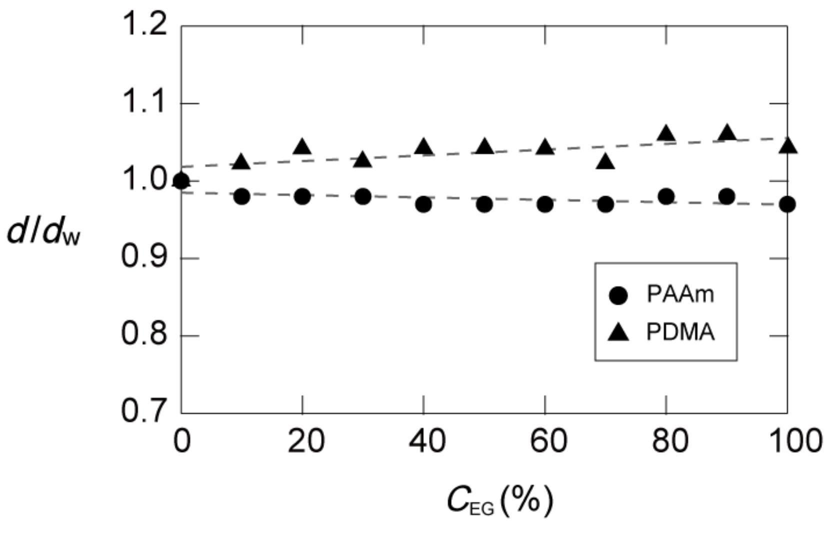

Figure S4 Equilibrium swelling ratios for two kinds of gels at various values of C_{EG}.

C. Estimation of some parameters in adhesion contact theories

Figure S5 shows the Maugis parameter λ vs C_{EG} plot for three values of δ (sample: PAAm gel, E_2 = 6.3kPa). In Figure S6, a_0 and d_0 calculated based on JKR, DMT, and MD theories are presented. Figure S7 presents U_{de} at three values of δ and U_{el}, U_a, and $U_{de} = U_{el} + U_a$ at δ = 2nm, plotted against C_{EG}.

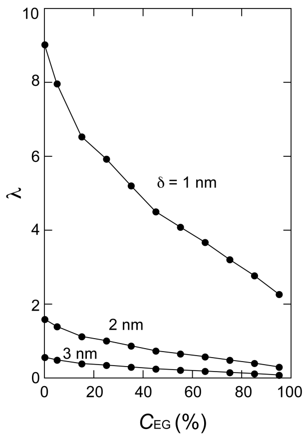

Figure S5 λ vs C_{EG} plot for three values of δ.

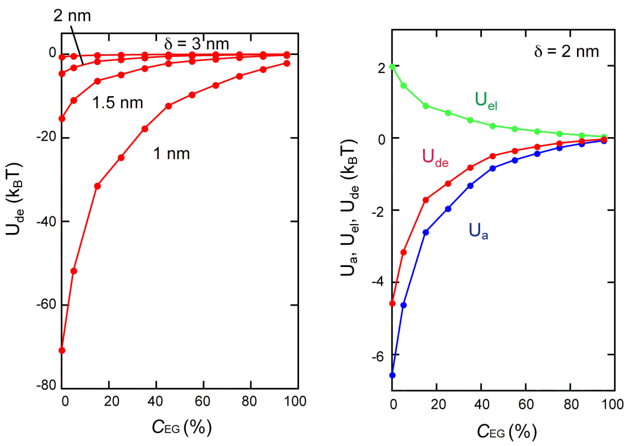

Figure S7 (left) $U_{de} = U_{el} + U_a$ at three values of δ. (right) U_{de}, U_{el}, and U_a plotted against C_{EG}.

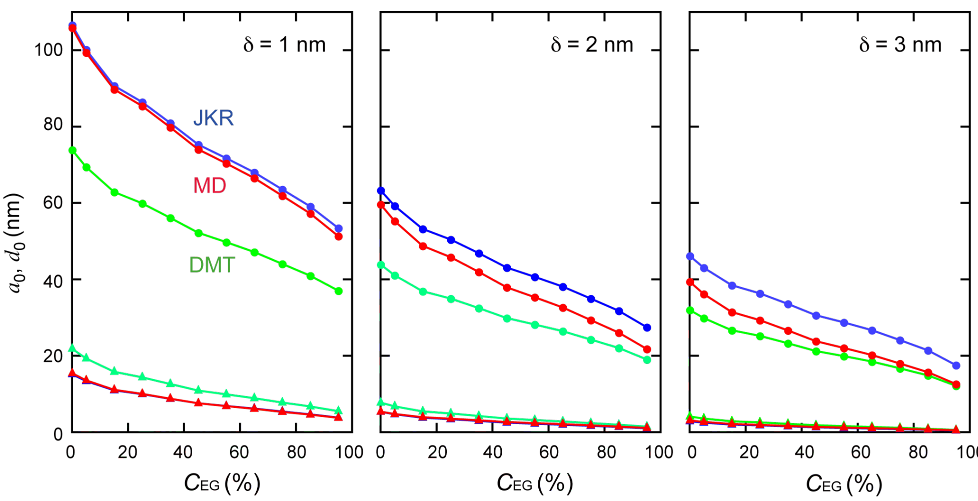

Figure S6 a_0 (circles) and d_0 (triangles) calculated based on JKR, MD, and DMT theories plotted against C_{EG} for three values of δ.