Electronic Supplementary Material (ESI) for Soft Matter.

Nanoparticle Adsorption Dynamics at Fluid Interfaces

Xiaoqing Hua, Michael A. Bevan, and Joelle Frechette**
Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, MD 21218
Email: mabevan@jhu.edu, jfrechette@jhu.edu

SUPPORTING INFORMATION

Derivation of the long-time limit

At long-time, when t→∞, the subsurface concentration, c_i, is approaching the bulk concentration, C_i. Thus the difference between the two concentrations can be obtained from Ward-Tordai equation (Eqn. (2) in main text)[1], given by:

$$\Delta c = C_i - c_i = \Gamma_i \sqrt{\frac{\pi}{4D_i t}} \quad . \tag{S1}$$

The Ward-Tordai model assumes that at any time, the species in sub-surface is in equilibrium with the interface.[2] Thus a relationship between surface excess, Γ_i and sub-surface concentration, c_i, can be obtained from Frumkin adsorption isotherm (Eqn. (4) in main text), given by:

$$d\Gamma_i = \frac{\Gamma_{i,\infty}\left(\Gamma_{i,\infty} - \Gamma_i\right)^2}{a_{L,i}\exp\left(K_i\Gamma_i / \Gamma_{i,\infty}\right)} \frac{1}{\Gamma_{i,\infty}^2 + K_i\Gamma_i\Gamma_{i,\infty} - K_i\Gamma_i^2} dc \quad . \tag{S2}$$

Following the same procedure as the one employed to extract the long-time limit for surfactant adsorption,[1] followed by incorporating the wetting EOS (Eqn. (6) in main text), the following $d\gamma$ over time can be obtained, given by:

$$\left.\frac{d\gamma}{dt^{-1/2}}\right|_{t\to\infty} = \left|\Delta E\right| \frac{\Gamma_i^2}{C_i} \frac{\Gamma_{i,\infty}\left(\Gamma_{i,\infty} - \Gamma_i\right)}{\Gamma_{i,\infty}^2 + K_i\Gamma_i\Gamma_{i,\infty} - K_i\Gamma_i^2} \sqrt{\frac{\pi}{4D_i}} \quad . \tag{S3}$$

Eqn S3 can be simplified using $\theta_i = \Gamma_i / \Gamma_{i,\infty}$, resulting in:

$$\gamma = \gamma_{eq} + \left(\left|\Delta E\right|\right)\left(\frac{1-\theta_{NP}}{1+K_{NP}\theta_{NP}\left(1-\theta_{NP}\right)}\right)\left(\frac{\Gamma_{NP}^2}{C_{NP}}\sqrt{\frac{\pi}{4D_{NP}t}}\right) \quad . \tag{S4}$$

Effects of all parameters on fitting dynamics of NP adsorption

The role of the different parameters on the dynamic data is shown in Figure S1 and Figure S2, for the adsorption of 5 nm NP dispersed in pH 11.0 solution and 10 nm NP dispersed in pH 11.7 solution. The corresponding parameters are listed in Table S1 and Table S2 respectively.

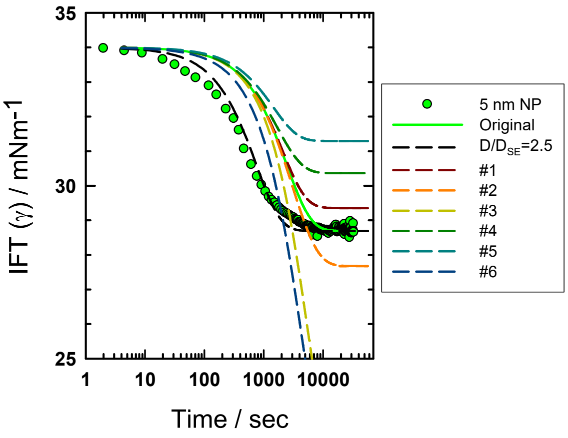

Figure S1. Dynamics of adsorption of 5 nm 3.5×10^{11} /mL NPs dispersed in 5 mM pH 11.0 KOH solution, with the corresponding fitting parameters shown in Table S1.

Table S1. Parameters for the prediction of the dynamics of adsorption of 5 nm 3.3×10^{11} /mL NPs dispersed in 5 mM pH 11.0 KOH solution, with the highlighted parameters adjusted compared to the original parameters.

#	r_{NP} (nm)	$a_{L,NP}$ $(\#/mL)$	K_{NP}	$\eta_{NP,\infty}$
Original	3.5	1.6×10^{12}	0	0.85
1	3.5	1.6×10^{12}	***1***	0.85
2	3.5	1.6×10^{12}	***-1***	0.85
3	3.5	***0.5×10¹²***	0	0.85
4	3.5	***2.5×10¹²***	0	0.85
5	**2.5**	1.6×10^{12}	0	0.85
6	**5.5**	1.6×10^{12}	0	0.85

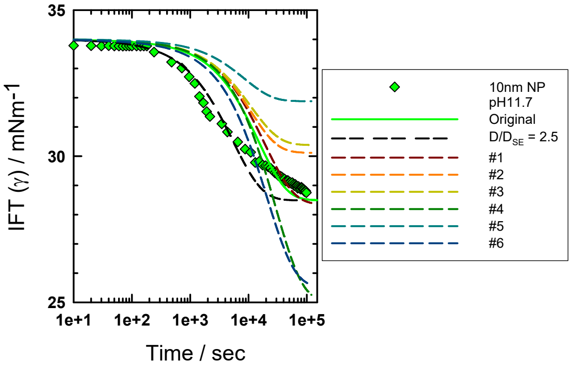

Figure S2. Dynamics of adsorption of 10 nm 3.7×10^{11} /mL NPs dispersed in pH 11.7 5 mM KOH solution, with the corresponding fitting parameters shown in Table S2.

Table S2. Parameters for the prediction of the dynamics of adsorption of 10 nm 3.7×10^{11} /mL NPs dispersed in pH 11.7 5 mM KOH solution, with the highlighted parameters adjusted compared to the original parameters.

#	$r_{NP}\ (nm)$	$a_{L,NP}\ (\#/\,mL)$	K_{NP}	$\eta_{NP,\infty}$
Original	6.0	2.7×10^{12}	-1.6	0.95
1	6.0	2.7×10^{12}	***-2.5***	0.95
2	6.0	2.7×10^{12}	***0***	0.95
3	6.0	$\boldsymbol{3.5\times10^{12}}$	-1.6	0.95
4	6.0	$\boldsymbol{1.5\times10^{12}}$	-1.6	0.95
5	***4.0***	2.7×10^{12}	-1.6	0.95
6	***8.0***	2.7×10^{12}	-1.6	0.95

Adjusting the NP Diffusivity

We varied the diffusivity to obtain better predictions for NP adsorption dynamics, as shown in dashed lines in Figure 3-4 in the main text. The diffusivities used compared to the Stokes-Einstein diffusivity are shown below.

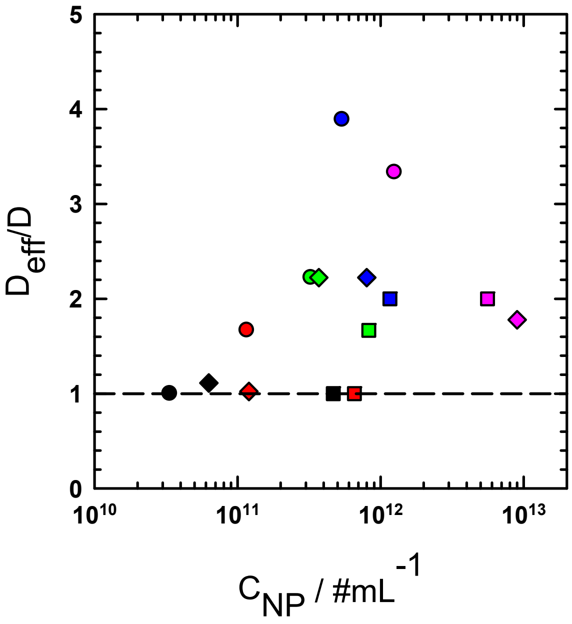

Figure S3. Value of the diffusivity (D_{eff}) if used as a fitting parameter to predict dynamic IFT in Figure 3 in the main text for 5 nm NP dispersed in 5 mM KOH solutions at pH 11.0 (circles), 5 nm NP dispersed in 5 mM KOH solutions at pH 11.7 (squares), and 10 nm NP dispersed in 5 mM KOH solutions at pH 11.7 (diamonds).

Pressure isotherms of TPeA$^+$ adsorption

The pressure isotherms of TPeA$^+$ in solution with total ionic strength of 5 mM solution at pH 11.0 and pH 11.7 are shown in Figure S4. The lines represents fits to the equilibrium pressure isotherms, with parameters listed in Table 2 in the main text.[3]

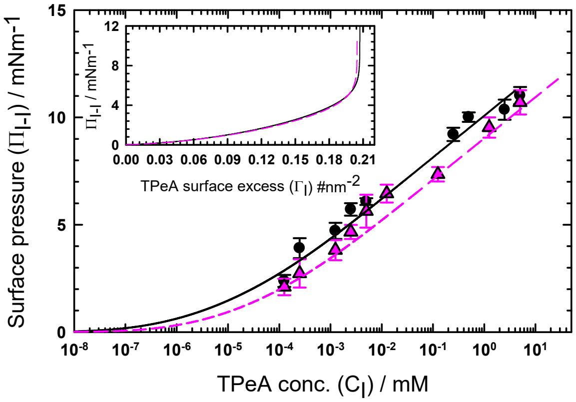

Figure S4. Surface pressure of TPeA$^+$ ions in 5 mM, pH11.0 solution (pink triangles) and pH11.7 solution (black circles) measured via pendant drop shape analysis. The lines are the corresponding fits using Frumkin model described by Eqns. (4)–(5) in the main text. The fitting parameters are listed in Table 2 in the main text. Inset is the predicted EOS for TPeA$^+$ for the same conditions using Eqn. (5) in the main text also with parameters listed in Table 2.

References

1. V. B. Fainerman, A. V. Makievski and R. Miller, *Colloids Surf., A*, 1994, **87**, 61-75.
2. A. F. H. Ward and L. Tordai, *J. Chem. Phys.*, 1946, **14**, 453-461.
3. V. L. Kolev, K. D. Danov, P. A. Kralchevsky, G. Broze and A. Mehreteab, *Langmuir*, 2002, **18**, 9106-9109.