Supporting Information

Role of electrostatic interactions on the adsorption kinetics of nanoparticles at fluid-fluid interfaces

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Adsorption kinetics of nanoparticle at interface:

The early time data for 1wt% suspension containing different concentration of NaCl modeled using modified Ward and Tordai model is shown Fig S2.

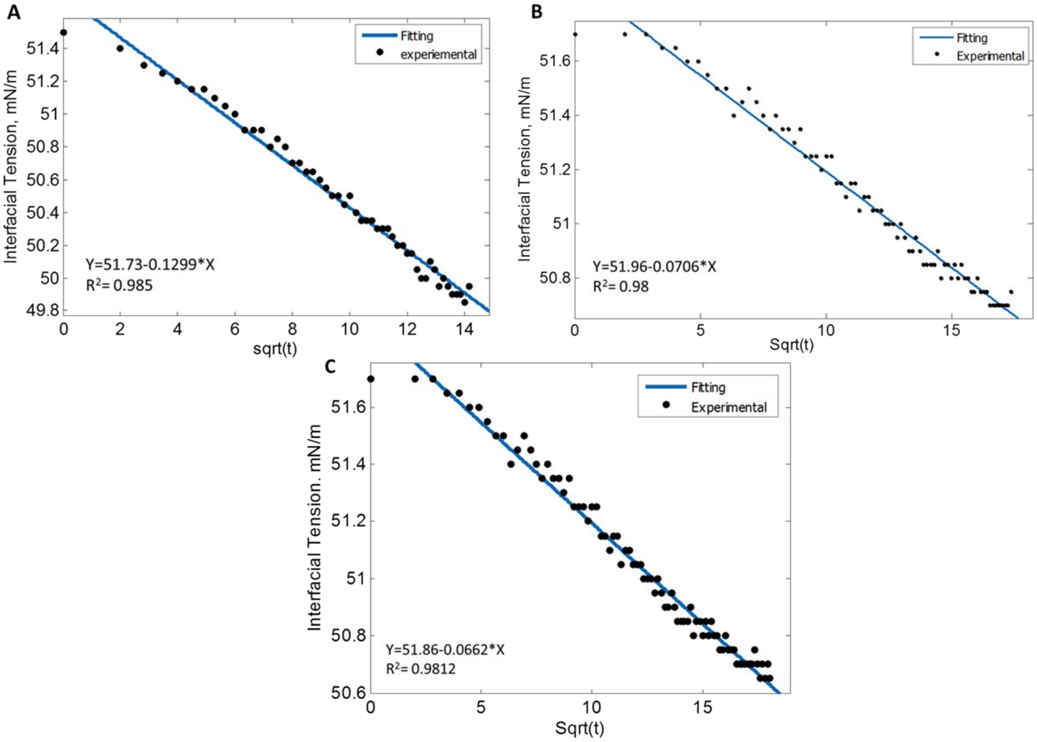

Fig S1: The early time DST plot between interfacial tension (γ) Vs $\sqrt{t}$. Suspension contains 1wt % silica particles with different salt concentration A) 0.05 M B) 0.005M C) 0.001M

Equilibrium coverage of particles at interface:

The equilibrium surface coverage of particles at interface is obtained by equating the chemical potential of particles in the bulk and with those absorbed at the interface. The chemical potential of the particles in the bulk is [1]

$$\frac{\mu_{bulk}}{k_B T} = \ln\left(\frac{V_w}{V_p}\right) + \ln\left(\phi_b\right) + \left(\frac{4\pi r^2 \gamma_{pw}}{k_B T}\right) \tag{1}$$

Where, V_w is droplet volume, V_p is particle volume, ϕ_b is particles volume fraction in the bulk, r is particle radius, γ_{pw} is particle-water interfacial tension, k_B is Boltzmann constant and T is the temperature. Similarly, the chemical potential of the particles at interface is

$$\frac{\mu_{\text{int}}}{k_B T} = \ln\left(\frac{A_i}{A_c}\right) + \ln\left(\phi_{i}\right) + \left(\frac{A_{pw}\gamma_{pw} + A_{po}\gamma_{po} - A_c\gamma_{ow}}{k_B T}\right) + \left(\frac{E_{dd} + E_{coul}}{k_B T}\right) \tag{2}$$

Where, A_i is drop interfacial area, A_c is area occupied by the particle at interface, ϕ_{i} is particles area fraction at interface, A_{pw} is surface area of particle in water, A_{po} is surface area of particle in oil, γ_{po} is particle-oil interfacial tension, γ_{ow} is water-oil interfacial tension, E_{dd} is dipole-dipole interaction, and E_{coul} is coulomb interaction. At equilibrium the bulk chemical potential and interfacial chemical potentials are equal. The equilibrium chemical potential of the system is

$$\ln\left(\frac{V_w}{V_p}\right) + \ln\left(\phi_b\right) + \left(\frac{4\pi r^2 \gamma_{pw}}{k_B T}\right) = \ln\left(\frac{A_i}{A_c}\right) + \ln\left(\phi_{i}\right) + \left(\frac{A_{pw}\gamma_{pw} + A_{ow}\gamma_{ow} - A_c\gamma_{ow}}{k_B T}\right) + \left(\frac{E_{dd} + E_{coul}}{k_B T}\right) \tag{3}$$

$$\ln\left(\frac{V_w A_c \phi_b}{V_p A_i \phi_{i}}\right) = \left(\frac{4\pi r^2 \gamma_{pw} - A_{pw}\gamma_{pw} - A_{ow}\gamma_{ow} + A_c\gamma_{ow}}{k_B T}\right) + \left(\frac{E_{dd} + E_{coul}}{k_B T}\right) \tag{4}$$

$$\ln\left(\frac{V_w A_c \phi_b}{V_p A_i \phi_{i}}\right) = \left(\frac{\Delta E}{k_B T}\right) + \left(\frac{E_{dd} + E_{coul}}{k_B T}\right) \tag{5}$$

Where, $\Delta E = 4\pi r^2 \gamma_{pw} - \left(A_{pw}\gamma_{pw} + A_{ow}\gamma_{ow} - A_c\gamma_{ow}\right)$ is equal to the detachment energy of particle from interface.

$$\phi_{i}^{*} = \frac{N_i}{N_T} = \frac{\phi_i A_i}{A_c N_T} \tag{6}$$

$$\phi_b^{*} = \frac{N_b}{N_T} = \frac{\phi_b V_w}{V_p N_T} \tag{7}$$

Here, ϕ_{int}^{*} is ratio of number of particles at interface (N_i) to total number of particles (N_T) and ϕ_{bulk}^{*} is the ratio of the number of particles in the bulk (N_b) to the total number of particles (N_T). By substituting the eq (6) and (7) in eq (5)

$$\phi_{\mathrm{i}}^{*} = \phi_{b}^{*} \exp - \left(\left(\frac{\Delta E}{k_B T} \right) + \left(\frac{E_{dd} + E_{coul}}{k_B T} \right) \right) \tag{8}$$

From the particles conservation, eq (8) can be rewrite as

$$\phi_{\mathrm{i}}^{*} = \left(1 - \phi_{\mathrm{i}}^{*}\right) \exp - \left(\left(\frac{\Delta E}{k_B T} \right) + \left(\frac{E_{dd} + E_{coul}}{k_B T} \right) \right) \tag{9}$$

$$\phi_{\mathrm{i}}^{*} = \frac{1}{1 + \exp\left(\left(\frac{\Delta E}{k_B T} \right) + \left(\frac{E_{dd} + E_{coul}}{k_B T} \right) \right)} \tag{10}$$

In eq (10), the detachment energy of the particle is given by

$$\Delta E = \pi r^2 \gamma_{ow} \left(1 - \left|\cos\theta\right|\right)^2 \tag{11}$$

Here, θ is three phase contact angle of particle at interface. The dipole-dipole and coulomb interactions depend on the particle surface charge and the center-to-center distance between the particles, which in turn depends on surface coverage. Therefore the expression for the dipole-dipole and coulomb interactions are expressed in terms of surface coverage and surface charge density. When a charged particle is present at the interface, asymmetric distribution of charges across the interface leads to the formation of a dipole in the water side. The chemical potential due the dipole-dipole interaction is given by[2]

$$E_{dd} = \frac{z \pi r \sigma^2 L_D^2 y^{\frac{3}{2}}}{16 \varepsilon_{dipole} \varepsilon_0} \tag{12}$$

Where, z is the number of nearest neighbors in two dimensions, σ is the surface charge density, L_D is the Debye length, y is the ratio of surface coverage to maximum possible surface coverage in two dimension ($\phi_i / \phi_{\max}$), ε_0 is the permittivity of vacuum and ε_{dipole} is the weight average dielectric constant of the water and oil phases. Similarly, as some unscreened ions can be present at the oil/particle interface, long-range Coulomb repulsion between the particles at the interface originating through the oil phase are also considered.[3]

$$E_{coul} = \frac{3 z \pi r^3 \alpha^2 \sigma^2 \sqrt{y}}{8 \varepsilon_{oil} \varepsilon_0} \tag{13}$$

Here, α is the scaling factor which takes a value between 0 and 1. The scaling factor accounts for the effect of the charged species in the oil side. The van der Waals interactions are neglected as they are relatively weak at long distances. Eq (10) is solved for the equilibrium surface coverage by substituting the eq (13), (12), (11) and (6) in eq (10). The equilibrium surface coverage as a function of surface charge density and salt concentration is shown in Fig S2.

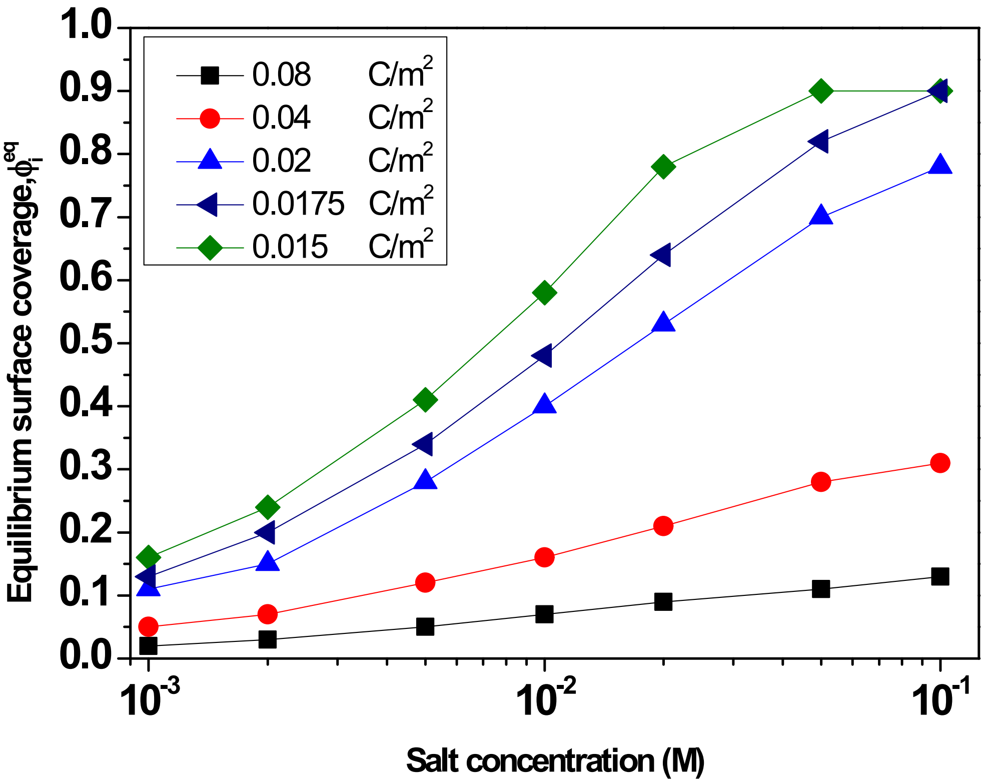

Fig S2: Surface coverage as a function of salt concentration at different surface charge density. Surface coverage is increasing with increasing salt concentration due to reduction in the Debye length. Similarly decreasing in surface charge also promotes more coverage at interface. The parameter values used in the calculations are, $r = 5$ nm, $\theta = 38^\circ$, $\gamma_{ow} = 52$ mN/m, $z = 6$, $\alpha = 0.1$, $\varepsilon_{dipole} = 41$, and $\varepsilon_{oil} = 2$.

Reference:

1. F. Reincke, W. K. Kegel, H. Zhang, M. Nolte, D. Wang, D. Vanmaekelbergh and H. Möhwald, *PCCP*, 2006, **8**, 3828-3835.
2. P. Pieranski, *Phys. Rev. Lett.*, 1980, **45**, 569.
3. R. Aveyard, J. H. Clint, D. Nees and V. N. Paunov, *Langmuir*, 2000, **16**, 1969-1979.