

## Distribution Potential at Small Liquid-Liquid Interfaces

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For the first time, the distribution potential at the oil/water interface is calculated for a small system with a small volume of one of the phases. Many authors are interested in the situation when the volume of organic phase is small in comparison with aqueous phase [1-14]. The analytical solution for a nanoheterogeneous system is obtained without assuming the electroneutrality in each phase. If the size of an oil droplet is comparable with the Debye screening length and the distribution potential exceeds  $kT/e_0$ , then the solution can be found numerically.

Let us consider a microemulsion with droplets of oil (D) in water (W). Let the radius of the droplet be equal  $R$  and the aqueous phase contain a uni-univalent electrolyte with concentration in the bulk equal to  $c_\infty$ . The electrolyte can partition into the oil droplet with partition coefficients for cations and anions  $P_c^{D/W}$  and  $P_a^{D/W}$ , respectively. If these values are not equal to each other, then the distribution potential builds up at the interface. To investigate the effect of geometry we shall use the Poisson-Boltzmann equation for electrical potential  $\phi$ , which is a function of radius  $r$ . The potential profile in the oil droplet and in surrounding aqueous media:

$$\phi_D(r) = \phi_0 \left[ 1 - \frac{R}{r} \frac{\frac{\sinh(\kappa_D r)}{\sinh(\kappa_D R)}}{1 + \frac{\kappa_W^2 (P_c^{D/W} + P_a^{D/W}) (\kappa_D R \coth(\kappa_D R) - 1)}{2\kappa_D^2 (\kappa_W R + 1)}} \right],$$

$$\phi_W(r) = \phi_0 \frac{R}{r} e^{-\kappa_W(r-R)} \left[ 1 - \frac{1}{1 + \frac{\kappa_W^2 (P_c^{D/W} + P_a^{D/W}) (\kappa_D R \coth(\kappa_D R) - 1)}{2\kappa_D^2 (\kappa_W R + 1)}} \right].$$

The parameter of most interest is the potential in the center of the droplet:

$$\phi_D(0) = \phi_0 \left[ 1 - \frac{\frac{\kappa_D R}{\sinh(\kappa_D R)}}{1 + \frac{\kappa_W^2 (P_c^{D/W} + P_a^{D/W}) (\kappa_D R \coth(\kappa_D R) - 1)}{2\kappa_D^2 (\kappa_W R + 1)}} \right].$$

The expression in the square brackets is always less than 1. Therefore, the potential in the oil droplet is always less than  $\phi_0$  and the value of the distribution potential would be established if the oil was present in macroscopic amount.

The potential depends on the droplet radius  $R$ . Let us consider two limiting cases for very small and very large radii. If  $R \rightarrow 0$ , then:

$$\phi_D(0) \approx \frac{\phi_0 R^2}{6} \left[ \kappa_D^2 + \kappa_W^2 (P_c^{D/W} + P_a^{D/W}) \right] \rightarrow 0.$$

If  $R \rightarrow \infty$ , then:

$$\phi_D(0) \approx \phi_0 \left[ 1 - \frac{2\kappa_D R e^{-\kappa_D R}}{1 + (P_c^{D/W} + P_a^{D/W}) \frac{\kappa_W}{\kappa_D}} \right] \rightarrow \phi_0.$$

In a very large droplet the distribution potential approaches its macroscopic value  $\phi_0$ .

There are two parameters that define this function. In this example, they are selected as:

$$\frac{\kappa_W (P_c^{D/W} + P_a^{D/W})}{2\kappa_D} = 1 \quad \text{and} \quad \frac{\kappa_D}{\kappa_W} = 5.$$

The potential is normalized by  $\phi_0$  and the droplet radius is normalized by the Debye parameter,  $\kappa_D$ . One can see the quadratic dependence of the potential on  $\kappa_D R$  at small radii. Half the maximum potential is achieved when  $\kappa_D R \approx 2$  and then the potential asymptotically approaches the maximum value of  $\phi_0$ .

In macroscopic phases, the distribution potential does not depend on a 1:1-electrolyte concentration if one neglects the difference in activity coefficients of ions. The same is true for small droplets. It can be easily seen if one introduces a dimensionless radius  $\rho = \kappa_D R$ .

$$\phi_D(0) = \phi_0 \left[ 1 - \frac{\frac{\rho}{\sinh(\rho)}}{1 + \frac{\kappa_W (P_c^{D/W} + P_a^{D/W}) (\rho \coth(\rho) - 1)}{2\kappa_D (R + \kappa_D / \kappa_W)}} \right]$$

Debye parameters  $\kappa_D$  and  $\kappa_W$  depend on electrolyte concentration as  $\sqrt{c}$ . However, these parameters appear in the equation only as a ratio of one to another. This ratio does not depend on concentration, and hence the distribution potential also does not depend on electrolyte concentration.

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