Lipid-Protein Interactions Alter Line Tensions and Domain Size Distributions in Lung Surfactant Monolayers

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Supporting Material

Derivation of Gibbs equation at a line interface:

A   E   D
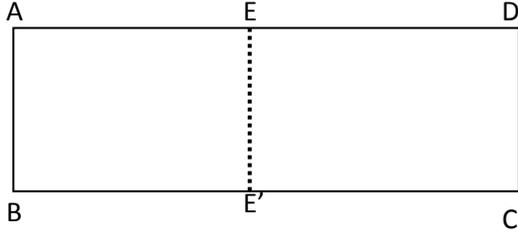
B   E'   C

Figure S1: Schematic of a two-dimensional liquid plane containing two phases separated by a line EE'

Consider a 2-d liquid plane (analogous to a 3-d liquid column) with I number of components in two phases l_o (α) and l_d (β) separated from each other by a line. The (surface) composition of the ith component in the l_o and l_d phases are c_{io} and c_{id}. If n_{io} and n_{id} stand for the total moles of the ith component in the two phases, then we can define a line excess (analogous to Gibbs surface excess) where the line excess n_i^x of the ith component should be

$$n_i^x = n_i^t - n_{io} - n_{id} \qquad\qquad (1)$$

where n_i^t is the total moles of the ith component for a given composition of the 2-d system.

The line excess internal energy : $E^x = E^t - E_o - E_d$ (2) where E_o is the internal energy in the a phase, E_d is the internal energy in the b phase, and E^t is the total internal energy.

Similarly, the entropy may be given by $S^x = S^t - S_o - S_d \qquad\qquad (3)$

For an open system:

$$dE^t = TdS^t - dW + \sum_1^i \mu_i dn_i \qquad\qquad (4)$$

where $dW = \pi_{so}dA_o + \pi_{sd}dA_d - \lambda dl \qquad\qquad (5)$

A_o and A_d stand for the actual area in the two phases, π_o and π_d are the surface pressures in the two phases, λ is the interfacial (line) tension, and μ_i is the chemical potential of the ith component. Substituting for dW (Eq. 5) in Eq. 4, we get an expression for the change in the total internal energy in terms of the surface pressures:

$$dE^t = TdS^t - \pi_{so}dA_o - \pi_{sd}dA_d + \lambda dl \quad + \sum_1^i \mu_i dn_i \qquad\qquad (6)$$

The changes in the internal energy in the idealized phases l_o and l_d may be expressed as:

$$dE_o = TdS_o - \pi_{so}dA_o + \sum_1^i \mu_i dn_i \qquad\qquad (7)$$

$$dE_d = TdS_d - \pi_{sd}dA_d + \sum_1^i \mu_i dn_i \qquad\qquad (8)$$

Note that the idealized systems have two two-dimensional phases without any physical interface.

The line excess internal energy difference may then be written as (Eq (6) −((7)+(8))):

$$dE^x = TdS^x + \lambda dl \quad + \sum_1^i \mu_i dn_i^x \tag{9}$$

Integrating equation 9, with T, λ, and μ_i constant gives:

$$E^x = TS^x + \lambda.l \quad + \sum_1^i \mu_i n_i^x \tag{10}$$

In general, if we differentiate equation 10, we get

$$dE^x = TdS^x + S^x dT + \lambda dl + l d\lambda \quad + \sum_1^i \mu_i dn_i^x + \sum_1^i n_i^x d\mu_i \tag{11}$$

Since (9) = (11) we get:

$$- l d\lambda = S^x dT \quad + \sum_1^i n_i^x d\mu_i \tag{12}$$

Dividing throughout by l we get

$$- d\lambda = \frac{S^x}{l} dT + \sum_1^i \frac{n_i^x}{l} d\mu_i \tag{13}$$

In equation 13, $\frac{S^x}{l} = S_\sigma^x$ is the line excess entropy per unit length and $\frac{n_i^x}{l} = \Gamma_i^x$ is the number of moles of the ith component per unit length. Then equation 13 may be rewritten as

$$- d\lambda = S_\sigma^x dT + \sum_1^i \Gamma_i^x d\mu_i \tag{14}$$

Since the magnitudes of S_σ^x and Γ_i^x are dependent on the position x of the line EE', we can fix the position of the line such that $n_1^t = n_{1o} + n_{1d}$ and $n_1^1 = 0$. Further, if the two phases are at the same temperature then, equation 14 can be converted to the form

$$- d\lambda = \sum_1^i \Gamma_i^1 d\mu_i \tag{15}$$

and $\Gamma_i^1 = \Gamma_i^x - \Gamma_1^x \frac{c_{io} - c_{id}}{c_{1o} - c_{1d}}$ is defined as the relative line excess of a species in solvent 1. Since $\mu_i = \mu_i^0 + RT \ln a_i$, substituting this in equation 15 gives

$$- d\lambda = RT \sum_1^i \Gamma_i^1 d \ln a_i = RT \sum_1^i \Gamma_i^1 f \, d \ln c_i$$

This is analogous to Gibbs Adsorption Equation[i] to a surface.

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[i] Chattoraj, D.K. and Birdi, K.S. Adsorption and the Gibbs Surface Excess. New York: Plenum Publishing Company, 1984