## Solubility and interfacial segregation of salts in ternary polyelectrolyte blends

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The contribution from ionic correlations is calculated using the Debye-Hückel Extended Mean Spherical Approximation (DHEMSA) closure on the Ornstein-Zernike equation, shown below:<sup>1–4</sup>

$$\hat{h}_{ik} = \hat{c}_{ik} + \sum_{l} \rho_l \hat{c}_{il} \hat{h}_{lk} \tag{1}$$

$$c_{ik} = \tilde{h_{ik}} - \ln(\tilde{h_{ik}} + 1) - \beta u_{ik}$$

$$\tag{2}$$

where  $\hat{c}$  and  $\hat{h}$  denote Fourier transforms of the direct and total correlation functions.

The liquid state approach allows for the consideration of charge ordering that is expected for sufficiently high densities and ionic correlation strengths ( $\Gamma$ ), which are neglected in the mean-field approach of non-linear Debye-Hückel theory. While DHEMSA closure closely resembles the hyper-netted chain (HNC) closure in its treatment of non-linear long-range electrostatics and short range repulsions, the algorithm has a superior convergence, and enables an efficient calculation of the pair correlation functions over a large parameter range of the liquid state, by an informed guess of h(r) instead of an iterative calculation approach used in HNC.<sup>1</sup>

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With this contribution, the total free energy can be written as:

$$f_{tot}(\phi_k, N_k, \chi_{kl}, f_{q,k}, a_m, \Gamma_{mn}) = f_{FH}(\phi_k, N_k, \chi_{kl}) + f_{PM}(\phi_k, f_{q,k}, a_m, \Gamma_{mn})$$
(3)

where indices k and l refer to different polymeric components (A, B, C), and m and n refer to ionic components (+, -). Here,  $a_m$  is the ion size, which is assumed to be equivalent for anions and cations in this particular study. In addition, it is assumed that all ions are monovalent, and that the anions on the polymer backbone are indistinguishable from dissociated salt anions. All cations are likewise assumed to be indistinguishable. The counterions to the charged backbone and salt anions are likewise indistinguishable. This simplification reduces all charge interactions to one that can be described using a single ion size and  $\Gamma$ , and the indices are subsequently dropped to give a free energy expression more specific to our system:

$$f_{tot} = \frac{\phi_A ln \phi_A}{N_A} + \frac{\phi_B ln \phi_B}{N_B} + \frac{\phi_C ln \phi_C}{N_C}$$
(4)

$$+ (f_{q,A}\phi_A + f_{q,C}\phi_C)ln(f_{q,A}\phi_A + f_{q,C}\phi_C) + f_{exc}(f_{q,A}\phi_A + f_{q,C}\phi_C, \Gamma)$$
(5)

Here,  $f_{q,A}\phi_A + f_{q,C}\phi_C$  represents the total amount of negative charge; to achieve electroneutrality, the same concentration of counterions is added.  $f_{q,A}$  is typically varied between 0.01 and 0.1.  $f_{q,C}$  is chosen to be 0 for the neutral solvent case, and 1 for the added salt case.  $f_{exc}(f_{q,A}\phi_A + f_{q,C}\phi_C, \Gamma)$  describes the excess energy due to ionic correlations, which favor phase separation as the total charge concentration  $f_{q,A}\phi_A + f_{q,C}\phi_C$  and ionic correlation strength  $\Gamma$  are increased.<sup>3</sup>

While a three-component blend can form four different phases  $\alpha, \beta, \gamma$ , and  $\delta, 5$  we only consider the  $\alpha$ - $\beta$  coexistence in this work by neglecting all Flory terms except for  $\chi_{AB}$ . The interactions governing the formation of other phases will be more rigorously investigated in a subsequent paper.<sup>2</sup> In the  $\alpha$ - $\beta$  coexistence, phase separation is driven by the interaction between A and B monomers. The coexistence line (or the phase boundary) is calculated by equating the chemical

potential of each component in  $\alpha$  (A-rich) and  $\beta$  (B-rich) phases. The chemical potential of each component k,  $\mu_k$ , is found using the following formula:<sup>6,7</sup>

$$\mu_k = \frac{\partial f_{tot}}{\partial \phi_k} + f_{tot} - \sum_k \phi_k \frac{\partial f_{tot}}{\partial \phi_k} \tag{6}$$

Here, k can be A, B, or C. Derivatives with respect to a particular  $\phi_k$  are to be taken with other volume fractions held constant. We assume that  $\chi_{AB}$ ,  $\chi_{BC}$ ,  $\chi_{AC}$  are independent of volume fraction.<sup>6</sup>

This gives us  $\mu_k$ :

$$\mu_A = \mu_{FH,A} + f_{q,A} ln(f_{q,A}\phi_A + f_{q,C}\phi_C) + f_{q,A} - f_{q,A}\phi_A - f_{q,C}\phi_C + \mu_{LS,A}$$
(7)

$$\mu_B = \mu_{FH,B} - f_{q,A}\phi_A - f_{q,C}\phi_C + \mu_{LS,B}$$
(8)

$$\mu_{C} = \mu_{FH,C} + f_{q,C} ln(f_{q,A}\phi_{A} + f_{q,C}\phi_{C}) + f_{q,C} - f_{q,A}\phi_{A} - f_{q,C}\phi_{C} + \mu_{LS,C}$$
(9)

where

$$\mu_{LS,k} = \frac{\partial f_{exc}}{\partial \phi_k} + f_{exc} - \sum_k \phi_k \frac{\partial f_{exc}}{\partial \phi_k} \tag{10}$$

and

$$\mu_{FH,k} = \frac{\ln\phi_k + 1}{N_k} - \sum_k \frac{\phi_k}{N_k} - \frac{1}{2} \sum_{o \neq p} (\phi_o - g_{o,k}) \chi_{op}(\phi_p - g_{p,k})$$
(11)

Here,  $g_{o,k} = 1$  if o = k, and  $g_{o,k} = 0$  if  $o \neq k$ .

We then solve for equilibrium compositions whose chemical potential in the two phases are equal; furthermore, the volume fractions all have to add up to 1 to satisfy the incompressibility condition.

$$\mu_A^{\alpha} = \mu_A^{\beta} \tag{12}$$

$$\mu_B^{\alpha} = \mu_B^{\beta} \tag{13}$$

$$\mu_C^{\alpha} = \mu_C^{\beta} \tag{14}$$

$$\phi_A^{\alpha} + \phi_B^{\alpha} + \phi_C^{\alpha} = \phi_A^{\beta} + \phi_B^{\beta} + \phi_C^{\beta} = 1$$
(15)

Once the equilibrium compositions are obtained, we use 1D self-consistent field theory (SCFT) to find the distribution of the three components across the  $\alpha - \beta$  interface using a discrete representation of the modified diffusion equation introduced by Edwards:<sup>8</sup>

$$\frac{\partial q(r,n)}{\partial n} = \frac{a^2}{6} \left( \frac{\partial^2 q(r,n)}{\partial r^2} \right) - \omega(r,n)q(r,n)$$
(16)

The variables r and n are continuous forms of discrete variables i and j used in this work, where i denotes discrete distance variable and j denotes the index of the repeat unit along a chain.<sup>7</sup> The width of each layer i corresponds to a, the statistical segment length of one repeat unit, which is defined so that  $R_g$ , the radius of gyration of a chain, is equal to  $(N_A/6a)^{1/2}$ . The mean field  $\omega(i, j)$  is a function of the composition along the chain, g(j), and the surrounding composition in the layer i,  $\phi(i)$ . Since all polymers are homopolymers and the composition does not vary along the chain,  $\omega(i, j)$  can be written as a function of only i.

$$\omega_k(i) = \omega_{p,k}(i) + \omega_{ext,k}(i) - k_B T \sum_k \frac{\phi_k(i)}{N_k} - \Delta\omega(i)$$
(17)

The first term,  $\omega_{p,k}(i)$  comes from enthalpic contributions characterized by Flory-Huggins pa-

rameters  $\chi_{AB}, \chi_{BC}, \chi_{AC}$ .

$$\omega_{p,A}(i) = \phi_B(i)(1 - \phi_A(i))\chi_{AB} - \phi_B(i)\phi_C(i)\chi_{BC} + \phi_C(i)(1 - \phi_A(i))\chi_{AC}$$
(18)

$$\omega_{p,B}(i) = \phi_A(i)(1 - \phi_B(i))\chi_{AB} - \phi_A(i)\phi_C(i)\chi_{AC} + \phi_C(i)(1 - \phi_B(i))\chi_{BC}$$
(19)

$$\omega_{p,C}(i) = \phi_A(i)(1 - \phi_C(i))\chi_{AC} - \phi_A(i)\phi_B(i)\chi_{AB} + \phi_B(i)(1 - \phi_C(i))\chi_{BC}$$
(20)

The second term,  $\omega_{ext,k}(i)$ , comes from electrostatic contributions characterized by  $\Gamma$ ,  $f_{q,A}$ , and  $f_{q,C}$ . This term can be calculated from the chemical potential  $\mu_k$ :

$$\omega_{ext,k}(i) = \mu_k(i) - \mu_{FH,k}(i) \tag{21}$$

The third term in equation 17 is the entropic contribution from the three components. The last term,  $\Delta\omega(i)$ , comes from the incompressibility constraint, where  $\zeta$  in equation 22 is inversely proportional to the bulk incompressibility of the system.

$$\frac{\Delta\omega(i)}{k_BT} = \zeta(1 - \sum_k \phi_k(i)) \tag{22}$$

In the presence of a field, the probability distribution functions  $q_k(i, j)$  can be obtained using recursion relationships that arise from the connectivity of the chains:

$$q_k(i,j) = \lambda_{-1} 1 q_k(i-1,j-1) + \lambda_0 q_k(i,j-1) +$$
(23)

$$\lambda_{+1}q_k(i+1,j-1)exp(-\omega_k(i)/k_BT)$$
(24)

where the  $\lambda_{-1}, \lambda_0, \lambda_{+1}$  are transition probabilites specific to the geometry of the system.<sup>6,7</sup> For homopolymers, only one  $q_k(i, j)$  is needed, as the composition profiles from the two ends of a single chain are indistinguishable.

Volume fraction profiles  $\phi_A(i), \phi_B(i), \phi_C(i)$  are obtained by summing the probability distribu-

tion functions  $q_k(i, j)$  from both ends:

$$\phi_k(i) = \frac{1}{N_k} exp(\mu_{bulk,k}/k_B T - 1) \sum_{j=1}^{N_k} q_k(i,j) q_k(i,N_k,j)$$
(25)

The new field is generated by the calculated volume fraction profile  $\phi_k(i)$ . The resulting probability distribution function and volume fraction profiles are iteratively and self-consistently solved with the boundary condition where the volume fraction profile at each end ( $i = 0, i = i_{\text{max}}$ ) corresponds to the bulk phase volume fraction and chemical potential  $\mu_{bulk,k}$  calculated from the phase diagram.

The interfacial tension is obtained by summing  $\Delta \omega$  over all of the lattice layers:<sup>9</sup>

$$\gamma = \sum_{i} L(i)\omega(i) \tag{26}$$

where L(i) is the number of lattice sites in layer *i*.

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