Supporting Materials

Influence of Cyclic Dimer Formation on the Equilibrium Behavior of Carboxylic Acids II - Cross Associating Systems

Jiří Janeček[1,2] and Patrice Paricaud[2*]
[1] Mines ParisTech, CTP, 35, rue Saint Honor 77305 Fontainebleau cedex, France.
[2] ENSTA-ParisTech, UCP, 828 Boulevard des Maréchaux, 91762 Palaiseau Cedex, France.
[*] email: patrice.paricaud@ensta-paristech.fr

Appendix I

The number densities of molecules non-bonded on one site (A or B), σ_{A_k} and σ_{B_k} and the number density of the free molecules σ_{0_k} at equilibrium are determined by minimizing the Helmholtz energy. The differentiation of the expression for the association Helmholtz energy (eq. (1) of the current article)

$$\frac{A^{assoc}}{Vk_BT} = \sum_i \left(\sigma_{\Gamma_i} \ln \frac{\sigma_{0_i}}{\sigma_{\Gamma_i}} + \sigma_{\Gamma_i} - \sigma_{A_i} - \sigma_{B_i} + \frac{\sigma_{A_i}\sigma_{B_i}}{\sigma_{0_i}} \right) - \sum_i \sum_j \sigma_{A_i}\sigma_{B_j}\Delta_{A_iB_j} - \frac{1}{2}\sum_i \sum_j \sigma_{0_i}\sigma_{0_j}\Phi_{ij}, \quad (1)$$

with respect to σ_{A_k}, σ_{B_k} and σ_{0_k} leads to the following three conditions for each component k

$$-1 + \frac{\sigma_{B_k}}{\sigma_{0_k}} - \sum_j \sigma_{B_j}\Delta_{A_kB_j} = 0, \quad (2)$$

$$-1 + \frac{\sigma_{A_k}}{\sigma_{0_k}} - \sum_i \sigma_{A_i}\Delta_{A_iB_k} = 0, \quad (3)$$

$$\frac{\sigma_{\Gamma k}}{\sigma_{0_k}} - \frac{\sigma_{A_k}\sigma_{B_k}}{\sigma_{0_k}^2} - \frac{1}{2}\sum_j \sigma_{0_j}\Phi_{kj} - \frac{1}{2}\sum_i \sigma_{0_i}\Phi_{ik} \;=\; 0. \tag{4}$$

Note that eq. 1 of the current article is expressed in terms of the homogenous scalar number densities after having performed some assumptions for the computation of the integrals $\Delta_{A_iB_k}$ and Φ_{ik}, while the original expression of the free energy is expressed in terms of number density distribution functions.[1,2] The minimization of the Helmholtz energy should then be obtained by performing functional differentiation with respect to the number density distributions. Here the minimization is performed with respect to the scalars σ_{A_k}, σ_{B_k} and σ_{0_k} for the sake of simplicity.

The two sums in the last equation are identical if $\Phi_{ij} = \Phi_{ji}$. One can express the equilibrium conditions (eqs. 2) to 4) in terms of the fractions of molecules non-bonded at a given site (A or B) ($X_{A_k} = \sigma_{A_k}/\sigma_{\Gamma k}$,$X_{B_k} = \sigma_{B_k}/\sigma_{\Gamma k}$, and in terms of the fraction of free molecules, $X_{0_k} = \sigma_{0_k}/\sigma_{\Gamma k}$), as

$$-1 + \frac{X_{B_k}}{X_{0_k}} - \rho\sum_j x_j X_{B_j}\Delta_{A_kBj} \;=\; 0, \tag{5}$$

$$-1 + \frac{X_{A_k}}{X_{0_k}} - \rho\sum_j x_j X_{Aj}\Delta_{AjBk} \;=\; 0, \tag{6}$$

$$\frac{1}{X_{0_k}} - \frac{X_{A_k}X_{B_k}}{X_{0_k}^2} - \rho\sum_j x_j X_{0_j}\Phi_{jk} \;=\; 0. \tag{7}$$

This set of conditions that determine the composition at equilibrium can be solved by using the numerical method described in Appendix II. In order to eliminate the integrals Δ_{A_iBj} and Φ_{ij} from the association contribution of the Helmholtz energy, one can multiply eqs. 2 and 3 by $\sigma_{A_k}/2$, and by $\sigma_{B_k}/2$, respectively, and sum the conditions over all components k. This leads to

$$\frac{1}{2}\sum_k \left(\sigma_{A_k} - \frac{\sigma_{A_k}\sigma_{B_k}}{\sigma_{0_k}}\right) = -\frac{1}{2}\sum_k\sum_j \sigma_{A_k}\sigma_{B_j}\Delta_{A_kBj}, \tag{8}$$

and

$$\frac{1}{2}\sum_k \left(\sigma_{B_k} - \frac{\sigma_{A_k}\sigma_{B_k}}{\sigma_{0_k}}\right) = -\frac{1}{2}\sum_k\sum_j \sigma_{Aj}\sigma_{B_k}\Delta_{AjBk}. \tag{9}$$

After changing the summation indices in the right-hand side of eqs. 8 and 9, and adding these two equations, one can express the second term of eq. 1) as

$$-\sum_i \sum_j \sigma_{A_i} \sigma_{B_j} \Delta_{A_i B j} = \sum_k \left(\frac{\sigma_{A_k}}{2} + \frac{\sigma_{B_k}}{2} - \frac{\sigma_{A_k} \sigma_{B_k}}{\sigma_{0_k}} \right) \tag{10}$$

By multiplying eq. 4 by σ_{0_k} and summing up for all components, one can show that

$$-\frac{1}{2} \sum_i \sum_j \sigma_{0_i} \sigma_{0_j} \Phi_{ij} = \frac{1}{2} \sum_i \left(\frac{\sigma_{A_i} \sigma_{B_i}}{\sigma_{0_i}} - \sigma_{\Gamma_i} \right). \tag{11}$$

By inserting eqs. 10 and 11 into eq. 1, the association contribution of the Helmholtz energy density can be written as

$$\frac{A^{assoc}}{V k_B T} = \sum_i \left(\sigma_{\Gamma_i} \ln \frac{\sigma_{0_i}}{\sigma_{\Gamma_i}} + \frac{\sigma_{\Gamma_i} - \sigma_{A_i} - \sigma_{Bi}}{2} - \frac{\sigma_{A_i} \sigma_{Bi}}{2 \sigma_{0_i}} \right). \tag{12}$$

The final relation for the association Helmholtz energy

$$\frac{A^{assoc}}{N k_B T} = \sum_i x_i \left(\ln X_{0_i} - \frac{X_{A_i}}{2} - \frac{X_{B_i}}{2} + \frac{X_{A_i} X_{B_i}}{2 X_{0_i}} + \frac{1}{2} \right), \tag{13}$$

is obtained by employing the fractions of non bonded molecules instead of the number densities in eq. 12, and by dividing eq. 12 by the total number density and replacing σ_{Γ_i} by $x_i \rho$.

An extension of the DBD association scheme to groups (molecules) containing more than two association sites can be done in a way analogous to the extension of the classical approach. For mixture containing components i, each with set of sites ia, the association Helmholtz energy is expressed as

$$\frac{A^{assoc}}{N k_B T} = \sum_i \sum_{ia} \left(\ln X_{ia} - \frac{X_{ia}}{2} + \frac{1}{2} \right) \tag{14}$$

For the DBD model analogous generalization can be written in terms of 'pairs of association sites',

$$\frac{A^{assoc}}{N k_B T} = \sum_i \sum_{ip} x_i \left(\ln X_{0_i} - \frac{X_{A_i}}{2} - \frac{X_{Bi}}{2} + \frac{X_{A_i} X_{Bi}}{2 X_{0_i}} + \frac{1}{2} \right) \tag{15}$$

where the inner summation runs over all pairs ip located at molecule of component i. The compressibility factor can be obtained from the derivative of the Helmholtz energy with respect to the total number density ρ. The association contribution to the compressibility factor is given by

$$Z^{assoc} = \rho\frac{\partial}{\partial\rho}\left(\frac{A^{assoc}}{Nk_BT}\right) = \sum_i x_i\left(\frac{X_{B_i}-X_{0_i}}{2X_{0_i}}\right)\frac{\partial X_{A_i}}{\partial\rho} + \\ + \sum_i x_i\left(\frac{X_{A_i}-X_{0_i}}{2X_{0_i}}\right)\frac{\partial X_{B_i}}{\partial\rho} + \sum_i x_i\left(\frac{2X_{0_i}-X_{A_i}X_{B_i}}{2X_{0_i}^2}\right).\frac{\partial X_{0_i}}{\partial\rho} \quad (16)$$

The association contribution to the chemical potential of component k is given by

$$\frac{\mu_k}{k_BT} = \frac{A^{assoc}}{Nk_BT} + (Z_{assoc}-1) + \frac{\partial}{\partial x_k}\left(\frac{A^{assoc}}{Nk_BT}\right) - \sum_j x_j\frac{\partial}{\partial x_j}\left(\frac{A^{assoc}}{Nk_BT}\right). \quad (17)$$

The derivatives of the association Helmholtz energy with respect to molar fractions, which are required for the calculation of the association contribution to the chemical potential, are given by

$$\frac{\partial}{\partial x_k}\left(\frac{A^{assoc}}{Nk_BT}\right) = \left(\ln X_{0_k} - \frac{X_{A_k}}{2} - \frac{X_{B_k}}{2} + \frac{X_{A_k}X_{B_k}}{2X_{0_k}} + \frac{1}{2}\right) + \\ + \sum_i x_i\left(\frac{X_{B_i}-X_{0_i}}{2X_{0_i}}\right)\frac{\partial X_{A_i}}{\partial x_k} + \sum_i x_i\left(\frac{X_{A_i}-X_{0_i}}{2X_{0_i}}\right)\frac{\partial X_{B_i}}{\partial x_k} + \\ \sum_i x_i\left(\frac{2X_{0_i}-X_{A_i}X_{B_i}}{2X_{0_i}^2}\right)\frac{\partial X_{0_i}}{\partial x_k}. \quad (18)$$

The partial derivatives of the fractions of molecules non bonded at a given site and of the fractions of free molecules, can be obtained by solving a set of $3n$ linear equations. This set of equations is obtained from the derivative of the equilibrium conditions (eqs. 5, 6 and 7) with respect to the total number density (compressibility factor) or with respect to a particular molar fraction (chemical potential), by keeping the remaining variables fixed. Note that the association strengths Δ_{A_iBj} and Φ_{ij} depend on both density and composition through the contact values of the radial distribution functions.

Appendix II

The fractions X_{A_k} and X_{B_k} and X_{0_k}, are the solutions of the equilibrium conditions (eqs. 5, 6 and 7 of the current article) that are linked together through the sums over all associating components. It is convenient to write these conditions as

$$\frac{X_{B_k}}{X_{0_k}} = 1 + \rho \sum_j x_j X_{B_j} \Delta_{A_k B_j}, \tag{19}$$

$$\frac{X_{A_k}}{X_{0_k}} = 1 + \rho \sum_j x_j X_{A_j} \Delta_{A_j B_k}, \tag{20}$$

$$0 = \frac{1}{X_{0_k}} - \frac{X_{A_k} X_{B_k}}{X_{0_k}^2} - \rho \sum_j x_j X_{0_j} \Phi_{jk}. \tag{21}$$

For compounds k which do not form doubly bonded dimers, i.e., for compounds k with $\Phi_{jk} = 0$ for all compounds j, eq. 21) reduces to $X_{0_k} = X_{A_k} X_{B_k}$. The first two equations then turn into the equilibrium conditions for the classical association approach:

$$\begin{aligned} X_{A_k} &= \left(1 + \rho \sum_j x_j X_{B_j} \Delta_{A_k B_j}\right)^{-1}, \\ X_{B_k} &= \left(1 + \rho \sum_j x_j X_{A_i} \Delta_{A_j B_k}\right)^{-1}. \end{aligned} \tag{22}$$

This set of equations is solved by using an iterative self-substitution procedure: The left-hand side is taken as the new approximation that is inserted back into the right-hand side until the desired accuracy is reached. Thus, the new estimates of X_{A_k}/X_{0_k} and X_{B_k}/X_{0_k} for each component k are calculated as

$$\left(\frac{X_{B_k}}{X_{0_k}}\right)^{new} = 1 + \rho \sum_j x_j (X_{B_j})^{old} \Delta_{A_k B_j}, \tag{23}$$

$$\left(\frac{X_{A_k}}{X_{0_k}}\right)^{new} = 1 + \rho \sum_j x_j (X_{A_i})^{old} \Delta_{A_j B_k}. \tag{24}$$

Because of the non-trivial form of eq. 21), we proposed another self substitution iterative approach for X_{0_k}. By multiplying eq. 21) by X_{0_k} and inserting the new estimated values $\left(\frac{X_{A_k}}{X_{0_k}}\right)^{new}$ and $\left(\frac{X_{B_k}}{X_{0_k}}\right)^{new}$, one can consider the following quadratic equation with respect to $X_{0_k}^{new}$:

$$1 - \left[\left(\frac{X_{A_k}}{X_{0_k}}\right)^{new} \left(\frac{X_{B_k}}{X_{0_k}}\right)^{new} + \rho \sum_{i \neq k} x_i X_{0_i}^{old} \Phi_{ik}\right] X_{0_k}^{new} - \rho x_k \Phi_{kk} (X_{0_k}^{new})^2 = 0. \tag{25}$$

The quadratic equation has two real roots, and the only root between 0 and 1 is taken as the new estimated values of X_{0_k}. New estimates of X_{A_k} and X_{B_k} are then obtained from

$$(X_{A_k})^{new} = (X_{0_k})^{new} \left(\frac{X_{A_k}}{X_{0_k}} \right)^{new} . \tag{26}$$

The new values of X_{A_k} and X_{B_k} are reinserted into eqs. 23) and 24) until convergence is reached. For compounds that do not form DBD, the new estimates of X_{A_k} and X_{B_k} are directly obtained at the first iteration step, because of the relation $X_{0_k} = X_{A_k} X_{B_k}$.

The initial values for X_{A_k} and X_{B_k} are obtained from the solutions of the classical 2B association term, by using $\Phi_{ij} = 0$ for all components. The initial value for X_{0_k} is then given by $X_{0_i} = X_{A_i} X_{B_i}$. We have tested the procedure to a prototype mixture of six associating compounds forming DBDs, with different values of bonding energy and volume such that $X_{A_k} > 0.99$ for some components and $X_{A_k} < 0.01$ for some others. Convergence was reached with less than 100 iterations.

References

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