

Supporting Information

Influence of Solute Association on the Phase Behavior of 12-Hydroxystearic Acid/*n*-Alkane Solutions

Tzu-Yu Lai^a †, Fardin Khabaz^{a,b}, and Kevin A. Cavicchi^{a*}

^a School of Polymer Science and Polymer Engineering, University of Akron, Akron, OH, 44325, United States

^b Department of Chemical, Biomolecular, and Corrosion Engineering, University of Akron, Akron, OH, 44325, United States

† Current address: 3M Company, St. Paul, MN 55144, United States

*Corresponding Author: kac58@uakron.edu

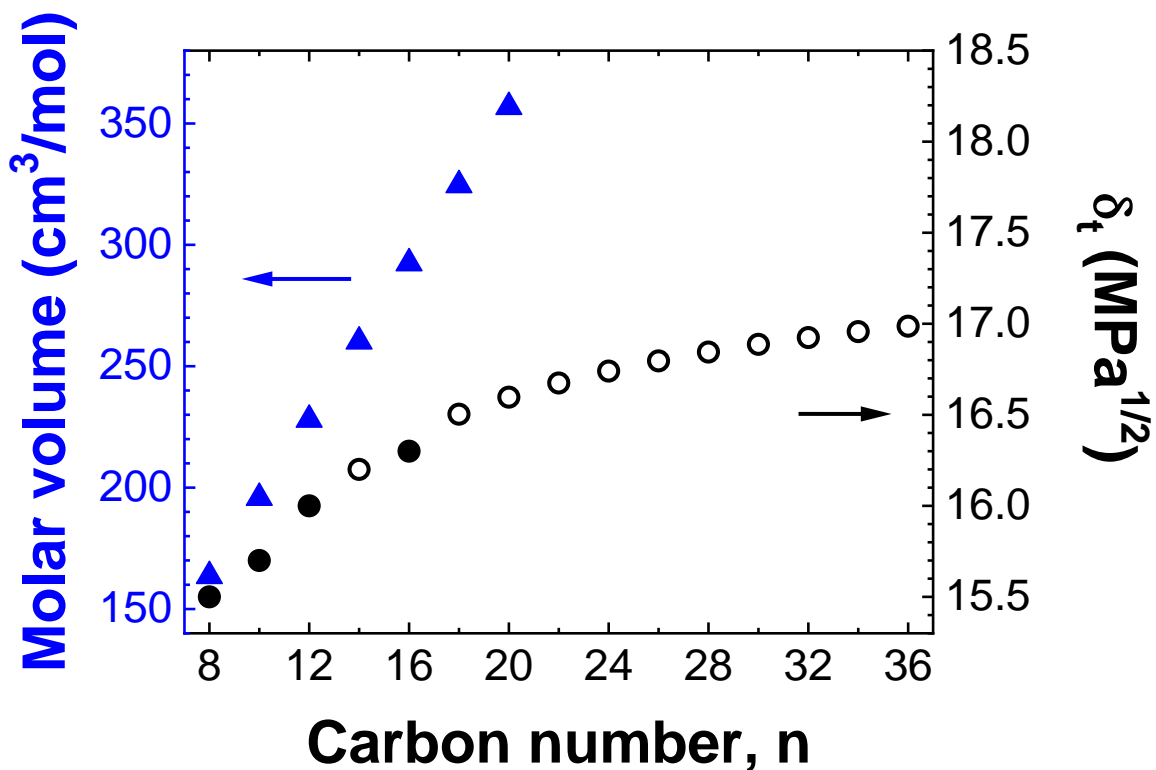


Figure S1. Molar volume (blue triangles) and total Hansen solubility parameter (δ_t , black circles) vs. the number of carbons in *n*-alkane backbone. The black, filled circles are tabulated values, while the open black circles and blue triangles were calculated by group contribution method.¹

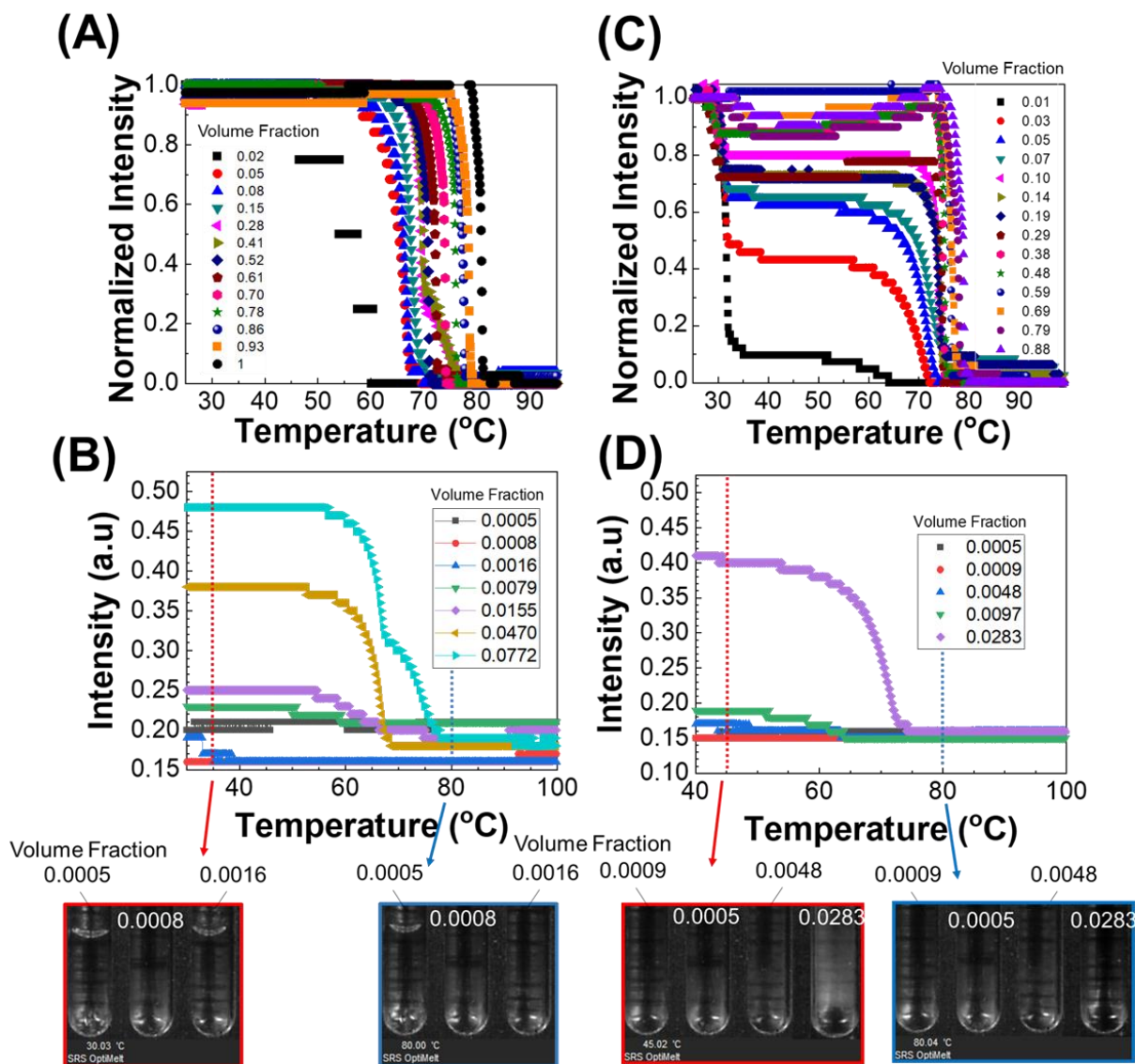


Figure S2. Light intensity changes of (a and b) 12HSA/decane and (c and d) 12HSA/octadecane mixtures measured by cloud point apparatus at a heating rate of 2°C/min. The transition from (c) around 32°C is related with the melting of octadecane crystals. (b and d) highlight the light insensitivity at low concentration

Stearic Acid/Dodecane Liquidus Line

The melting point $T_{m,SA}$ vs. volume fraction of stearic acid (SA, ϕ_{SA}) for stearic acid in dodecane was fit to the following equation assuming stearic acid forms a carboxylic acid dimer at all measured concentrations,

$$T_{m,SA} = \frac{\left(\frac{\Delta H_{f,SA-dimer}^0}{R} + r_{SA-dimer} \phi_{SA}^2\right)}{\phi_{SA} - 1 - \ln \phi_{SA} + \frac{r_{SA-dimer}}{r_S} \phi_S - r_{SA-dimer} \phi_S^2 B + \frac{\Delta H_{f,SA-dimer}^0}{RT_{m,SA}^0}} \quad (S1)$$

where $\Delta H_{f,SA-dimer}^0 = 2\Delta H_{f,SA}^0 = 128,560$ J/mol based on the reported value of $\Delta H_{f,SA}^0$, $r_{SA-dimer}$ is the ratio of the molar volume of the SA-dimer to the reference volume (octane), $\phi_S = 1 - \phi_{SA}$ is the molar volume of the solvent, r_S is the ratio of the molar volume of dodecane to the reference volume (octane), A and B are the coefficient of the Flory-Huggins interaction parameter, R is the gas constant, and $T_{m,SA}^0$ is the melting point of pure stearic acid, taken as 344.2 K from cloud point measurements. The resulting fit is shown in Figure S3.

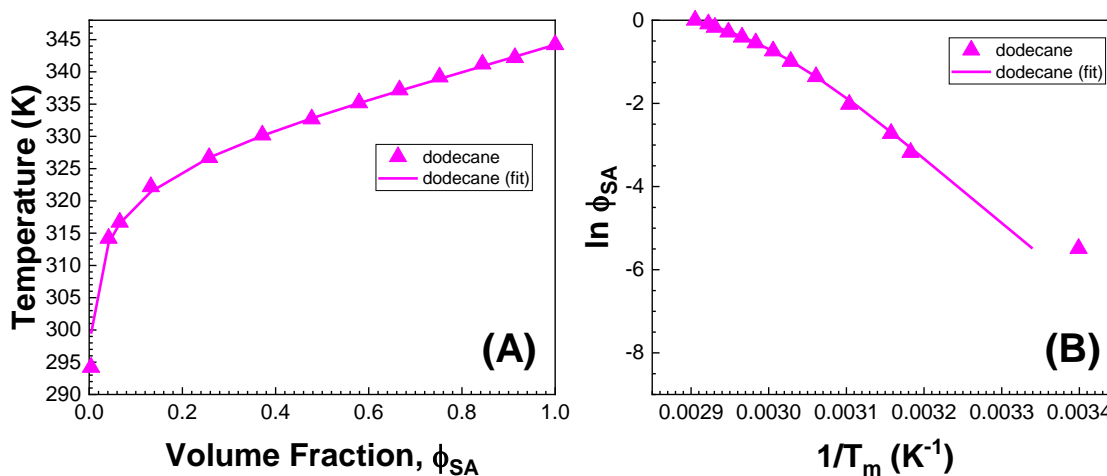


Figure S3. Fit of the liquidus line in stearic acid/dodecane solution using equation 12 with $B = 0$ and the other fitting constants given in Table 1 of the manuscript. The data points were previously reported in ref. 3. Adapted with permission from ref. 3 Copyright 2018 American Chemical Society.

Derivation of Attenuated Associated Solution Model

The following derivation follows derivations previously presented by Flory,⁴ Acree,⁵ and Painter et al.^{6,7} The results for the free energy of mixing and the attenuated association model are identical to those presented by Painter et al. and the derivation steps are presented here for completeness. The general equations for the free energy of mixing and liquidus line are derived first followed by specific equations using the attenuated association model. This would allow the reader to adapt this model to other associated solute models. The main idea is that the free energy of mixing expression for mixing an associated compound A and a solvent B is divided into a chemical contribution describing the free energy contributions due to the variation in the degree of association of compound A when mixing with solvent B and a physical contribution describing the non-specific interactions in mixtures compound A and solvent B.

The chemical contribution to the free energy change between the mixture of the associated compound A and solvent B from the pure liquid, where the pure liquid A has the same composition (i.e. molecular weight distribution) of associated species as the mixed phase is,

$$\frac{\Delta G^{m,ch}}{RT} = \sum_i n_{A_i} \ln \phi_{A_i} + n_B \ln \phi_B \quad (S2)$$

where n_{A_i} and n_B are the mole fractions of the associated compound of degree of association i , where $i=1$ is the monomer, and the solvent, respectively, and ϕ_{A_i} and ϕ_B are the volume fractions of associated compound and solvent, respectively.

To compare systems using solvents of different sizes, the molar volume of each solvent, V_{A_i} and V_B , is normalized by a reference volume V_r where,

$$\frac{V_{A_i}}{V_r} = r_{A_i} \quad \text{and} \quad \frac{V_B}{V_r} = r_B \quad (S3-4)$$

The volume fractions of each component are given by,

$$\phi_{A,i} = \frac{r_{A_i} n_{A_i}}{\sum r_{A_i} n_{A_i} + r_B n_B} \quad \phi_B = \frac{r_B n_B}{\sum r_{A_i} n_{A_i} + r_B n_B} \quad (S5-6)$$

Plugging equations S5 and S6 into equation S2 gives the chemical contribution to the free energy of mixing as,

$$\frac{\Delta G^{m,ch}}{RT} = \sum_i n_{A_i} \ln \frac{r_{A_i} n_{A_i}}{\sum r_{A_i} n_{A_i} + r_B n_B} + n_B \ln \frac{r_B n_B}{\sum r_{A_i} n_{A_i} + r_B n_B} \quad (S7)$$

The chemical potential of component A_i is given by,

$$\left(\frac{\mu_{A_i} - \mu_{A_i}^*}{RT} \right)^{ch} = \frac{\partial \left(\frac{\Delta G^{m,ch}}{RT} \right)}{\partial n_{A_i}} \quad (S8)$$

Where $\mu_{A_i}^*$ is the chemical potential of the pure liquid A with the same composition as in the mixed phase.

Writing out equation S7 with a separate term for component A_i gives,

$$\frac{\Delta G^{m,ch}}{RT} = n_{A_i} \ln \frac{r_{A_i} n_{A_i}}{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B} + \sum_{j \neq i} n_{A_j} \ln \frac{r_{A_j} n_{A_j}}{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B} + \quad (S9)$$

$$n_B \ln \frac{r_B n_B}{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B}$$

Differentiating equation S9 with respect to ∂n_{A_i} gives,

$$\left(\frac{\mu_{A_i} - \mu_{A_i}^{\bullet}}{RT} \right)^{ch} = \ln \phi_{A_i} + n_{A_i} \frac{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B}{r_{A_i} n_{A_i}} \left(\frac{r_{A_i} (r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B) - r_{A_i} (r_{A_i} n_{A_i})}{(r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B)^2} \right) +$$

$$\sum_{j \neq i} n_{A_j} \frac{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B}{r_{A_j} n_{A_j}} \left(\frac{-r_{A_i} (r_{A_j} n_{A_j})}{(r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B)^2} \right) +$$

$$n_B \frac{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B}{r_B n_B} \left(\frac{-r_{A_i} (r_B n_B)}{(r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B)^2} \right) \quad (S10.1)$$

Through a series of algebraic manipulations equation S10.1 is reduced to equation S10.6,

$$\left(\frac{\mu_{A_i} - \mu_{A_i}^{\bullet}}{RT} \right)^{ch} = \ln \phi_{A_i} + \left(\frac{(\sum r_{A_j} n_{A_j} + r_B n_B)}{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B} \right) + \sum_{j \neq i} n_{A_j} \left(\frac{-r_{A_i}}{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B} \right) +$$

$$n_B \left(\frac{-r_{A_i}}{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B} \right) \quad (S10.2)$$

$$\left(\frac{\mu_{A_i} - \mu_{A_i}^{\bullet}}{RT} \right)^{ch} = \ln \phi_{A_i} + \left(\frac{(\sum r_{A_j} n_{A_j} + r_B n_B - r_{A_i} n_{A_i} + r_{A_i} n_{A_i})}{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B} \right) + \sum_{j \neq i} \left(\frac{-n_{A_j} r_{A_i}}{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B} \right) +$$

$$n_B \left(\frac{-r_{A_i}}{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B} \right) \quad (S10.3)$$

$$\left(\frac{\mu_{A_i} - \mu_{A_i}^{\bullet}}{RT} \right)^{ch} = \ln \phi_{A_i} + 1 - \phi_{A_i} - r_{A_i} \sum_{j \neq i} \frac{\phi_{A_j}}{r_{A_j}} - \frac{r_{A_i}}{r_B} \phi_B \quad (S10.4)$$

$$\left(\frac{\mu_{A_i} - \mu_{A_i}^{\bullet}}{RT} \right)^{ch} = \ln \phi_{A_i} + 1 - \frac{r_{A_i}}{r_{A_i}} \phi_{A_i} - r_{A_i} \sum_{j \neq i} \frac{\phi_{A_j}}{r_{A_j}} - \frac{r_{A_i}}{r_B} \phi_B \quad (S10.5)$$

$$\left(\frac{\mu_{A_i} - \mu_{A_i}^{\bullet}}{RT}\right)^{ch} = \ln\phi_{A_i} + 1 - r_{A_i} \sum_j \frac{\phi_{A_j}}{r_{A_j}} - \frac{r_{A_i}}{r_B} \phi_B \quad (\text{S10.6})$$

The volume of 1 true mole of solution, V , is given by,

$$\frac{1}{V} = \sum_i \frac{\phi_{A_i}}{r_{A_i} V_r} + \frac{\phi_B}{r_B V_r} \quad (\text{S11})$$

Equation S11 may be rearranged to,

$$\frac{V_r}{V} = \sum_i \frac{\phi_{A_i}}{r_{A_i}} + \frac{r_B \phi_B}{r_B} \quad (\text{S12})$$

Plugging equation S12 into equation S10.6 gives

$$\left(\frac{\mu_{A_i} - \mu_{A_i}^{\bullet}}{RT}\right)^{ch} = \ln\phi_{A_i} + 1 - \frac{r_{A_i} V_r}{V} \quad (\text{S13})$$

When mixing pure compound A with solvent B, the molecular weight distribution shifts to minimize the free energy. To correctly describe the free energy of these mixtures, the chemical potential of component A_i needs to be in reference to the pure liquid of compound A, where the volume fraction of component A_i is not equal to its volume fraction in the mixed phase (i.e. standard state). For the pure liquid in the standard state, the solution volume is,

$$\frac{1}{V^o} = \sum_i \frac{\phi_{A_i}^o}{r_{A_i} V_r} \quad (\text{S14})$$

Where the superscript o represents the standard state.

The chemical potential change of the liquid going from the pure liquid with the same composition in the mixture to the pure liquid in the standard state is,

$$\left(\frac{\mu_{A_i}^o - \mu_{A_i}^{\bullet}}{RT}\right)^{ch} = \ln\phi_{A_i}^o + 1 - \frac{r_{A_i} V_r}{V^o} \quad (\text{S15})$$

Subtracting equation S15 from equation S13 gives the chemical potential change for component A_i from the standard state to the mixture as,

$$\left(\frac{\mu_{A_i} - \mu_{A_i}^o}{RT}\right)^{ch} = \ln\left(\frac{\phi_{A_i}}{\phi_{A_i}^o}\right) - \frac{r_{A_i} V_r}{V} + \frac{r_{A_i} V_r}{V^o} \quad (\text{S16})$$

Equation S16 describes the chemical contribution to the chemical potential. The physical contribution to the chemical potential can be added using a composition independent interaction parameter, such that overall free energy of mixing is given by

$$\frac{\Delta G^m}{RT} = \sum_i n_{A_i} \ln\phi_{A_i} + n_B \ln\phi_B + n_B \phi_{A\chi} \quad (\text{S17})$$

The physical contribution of the chemical potential of component A_i is given by,

$$\left(\frac{\mu_{A_i} - \mu_{A_i}^{\circ}}{RT}\right)^{ph} = \frac{\partial(n_B \phi_A \chi)}{\partial n_{A_i}} = \frac{\partial}{\partial n_{A_i}} \left(n_B \frac{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j}}{r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B} \chi \right) \quad (S18.1)$$

$$= n_B \frac{r_{A_i} (r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B) - r_{A_i} (r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j})}{(r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B)^2} \chi \quad (S18.2)$$

$$= r_{A_i} \frac{n_B^2}{(r_{A_i} n_{A_i} + \sum r_{A_j} n_{A_j} + r_B n_B)^2} \chi \quad (S18.3)$$

$$= r_{A_i} \phi_B^2 \chi \quad (S18.4)$$

Following equations 13-16, the chemical potential change of component A on mixing from the standard state including both the chemical and physical contributions is,

$$\frac{\mu_{A_i} - \mu_{A_i}^{\circ}}{RT} = \ln \left(\frac{\phi_{A_i}}{\phi_{A_i}^{\circ}} \right) - \frac{r_{A_i} V_r}{V} + \frac{r_{A_i} V_r}{V^{\circ}} + r_{A_i} \phi_B^2 \chi \quad (S19)$$

The chemical potential of component A may be written using the result of Prigogine,⁸

$$\mu_A = \mu_{A_1} \quad (S20)$$

Using equations S19 and S20, the chemical potential change of component A from the pure liquid to the mixture is,

$$\frac{\mu_A - \mu_A^{\circ}}{RT} = \ln \left(\frac{\phi_{A_1}}{\phi_{A_1}^{\circ}} \right) - \frac{r_{A_1} V_r}{V} + \frac{r_{A_1} V_r}{V^{\circ}} + r_{A_1} \phi_B^2 \chi \quad (S21)$$

The liquidus line is given by,

$$\frac{\mu_A - \mu_A^{\circ}}{RT_{m,A}} = -\frac{\Delta H_{f,A}^{\circ}}{R} \left(\frac{1}{T_{m,A}} - \frac{1}{T_{m,A}^{\circ}} \right) \quad (S22)$$

Where $T_{m,A}$ and $T_{m,A}^{\circ}$ are the melting points of component A of the mixture and the pure compounds, respectively.

Substituting in equation S22 into equation S21 gives a relationship for the melting temperature of component A as a function ϕ_B as,

$$\frac{1}{T_{m,A}} - \frac{1}{T_{m,A}^{\circ}} = -\frac{R}{\Delta H_{f,A}^{\circ}} \left(\ln \left(\frac{\phi_{A_1}}{\phi_{A_1}^{\circ}} \right) - \frac{r_{A_1} V_r}{V} + \frac{r_{A_1} V_r}{V^{\circ}} + r_{A_1} \phi_B^2 \chi \right) \quad (S27)$$

This is a general equation for the liquidus line. To fit experimental data either additional data or a model for molecular weight distribution of ϕ_A vs. composition is needed for the values of ϕ_{A_1} vs. ϕ_B and $\phi_{A_1}^{\circ}$. An attenuated association model is presented that is a modification of a continuous association model.

The reaction equilibrium for a continuous association model in terms of concentration is,

$$C_{A_i} + C_{A_1} \rightleftharpoons C_{A_{i+1}} \quad (\text{S28})$$

The associated equilibrium constant is,

$$K' = \frac{C_{A_{i+1}}}{C_{A_i} C_{A_1}} \quad (\text{S29})$$

This can be expressed in terms of volume fraction using

$$\phi_i = \frac{n_i V_i}{V} = C_i V_i \quad (\text{S30})$$

Substituting in $C_{A_i} = \phi_{A_i}/V_{A_i}$ into equation S29 gives,

$$K' = \frac{\phi_{A_{i+1}}/V_{A_{i+1}}}{(\phi_{A_i}/V_{A_i})(\phi_{A_1}/V_{A_1})} = \frac{\phi_{A_{i+1}}}{\phi_{A_i} \phi_{A_1}} \frac{V_{A_1} V_{A_1} i}{V_{A_1} (i+1)} = \frac{\phi_{A_{i+1}}}{\phi_{A_i} \phi_{A_1}} \frac{i}{i+1} V_{A_1} \quad (\text{S31})$$

Normalizing K' by the molar volume of the monomer gives,

$$K = \frac{K'}{V_{A_1}} = \frac{\phi_{A_{i+1}}}{\phi_{A_i} \phi_{A_1}} \frac{i}{i+1} \quad (\text{S32})$$

An attenuated association model is given by

$$\frac{K}{i+1} = \frac{\phi_{A_{i+1}}}{\phi_{A_i} \phi_{A_1}} \frac{i}{i+1} \quad (\text{S33})$$

Solving for different concentrations gives,

$$\phi_{A_2} = K \phi_{A_1}^2 \quad (\text{S34})$$

$$\phi_{A_3} = \frac{K \phi_{A_1} \phi_{A_2}}{2} = \frac{K^2 \phi_{A_1}^3}{2} \quad (\text{S35})$$

$$\phi_{A_4} = \frac{K \phi_{A_1} \phi_{A_3}}{3} = \frac{K^3 \phi_{A_1}^4}{6} \quad (\text{S36})$$

By inspection of equations S34-S36 the general expression may be written,

$$\phi_{A_i} = \frac{K^{i-1} \phi_{A_1}^i}{(i-1)!} \quad (\text{S37})$$

The overall composition of component A, ϕ_A , is given by the summation of ϕ_{A_i} as,

$$\phi_A = \sum_{i=1} \phi_{A_i} = \sum_{i=1} \frac{K^{i-1} \phi_{A_1}^i}{(i-1)!} = \sum_{i=1} \frac{\phi_{A_1} (K \phi_{A_1})^{i-1}}{(i-1)!} = \sum_{i=0} \frac{\phi_{A_1} (K \phi_{A_1})^i}{(i)!} \quad (\text{S38})$$

The summation in equation S38 may be rewritten using the Taylor series expansion for the exponential function,

$$e^x = \sum_{i=0} \frac{x^i}{i!} \quad (\text{S39})$$

Applying this to equation S38 gives gives,

$$\phi_A = \phi_{A_1} \exp (K \phi_{A_1}) \quad (\text{S40})$$

Returning to the Flory-Huggins model, the main equations to use are equations S11 and S27

$$\frac{1}{T_{m,A}} - \frac{1}{T_{m,A}^o} = -\frac{R}{\Delta H_{f,A}^o} \left(\ln \left(\frac{\phi_{A_1}}{\phi_{A_1}^o} \right) - \frac{r_{A_1} V_r}{V} + \frac{r_{A_1} V_r}{V^o} + r_{A_1} \phi_B^2 \chi \right) \quad (\text{S27})$$

$$\frac{1}{V} = \sum_i \frac{\phi_{A_i}}{r_{A_i} V_r} + \frac{\phi_B}{r_B V_r} \quad (\text{S11})$$

Using equations S38 and S11, equation S11 may be rewritten as,

$$\frac{r_{A_1} V_r}{V} = \sum_{i=1} \frac{\phi_{A_i}}{i} + \frac{r_{A_1} \phi_B}{r_B} = \sum_{i=1} \frac{K^{i-1} \phi_{A_1}^i}{i(i-1)!} + \frac{\phi_B}{r_B} = \frac{1}{K} \sum_{i=1} \frac{K^i \phi_{A_1}^i}{i!} + \frac{r_{A_1} \phi_B}{r_B} \quad (\text{S41.1})$$

$$= \frac{1}{K} \sum_{i=0} \frac{K^i \phi_{A_1}^i}{i!} - 1 + \frac{r_{A_1} \phi_B}{r_B} = \frac{1}{K} (\exp(K \phi_{A_1}) - 1) + \frac{r_{A_1} \phi_B}{r_B} \quad (\text{S41.2})$$

Similarly, equation S11 in the case of $\phi_B = 1$ is,

$$\frac{r_{A_1} V_r}{V^o} = \sum_{i=1} \frac{\phi_{A_i}^o}{i} = \sum_{i=1} \frac{K^{i-1} \phi_{A_1}^o{}^i}{i(i-1)!} = \frac{1}{K} \sum_{i=1} \frac{(K \phi_{A_1}^o)^i}{i!} = \frac{1}{K} \sum_{i=0} \frac{(K \phi_{A_1}^o)^i}{i!} - 1 \quad (\text{S42.1})$$

$$= \frac{1}{K} (\exp(K \phi_{A_1}^o) - 1) \quad (\text{S42.2})$$

Plugging equations S41 and S42 into equation S27 gives an expression for the liquidus line as,

$$\frac{1}{T_{m,A}} - \frac{1}{T_{m,A}^o} = -\frac{R}{\Delta H_{f,A}^o} \left(\ln \left(\frac{\phi_{A_1}}{\phi_{A_1}^o} \right) - \frac{1}{K} \exp(K \phi_{A_1}) - \frac{r_{A_1} \phi_B}{r_B} + \frac{1}{K} \exp(K \phi_{A_1}^o) + r_{A_1} \phi_B^2 \chi \right) \quad (\text{S43})$$

Using $\chi = \frac{A}{T} + B$ and rearranging gives,

$$T_{m,A} = \frac{\left(\frac{\Delta H_{f,A}^o}{R} + r_{A_1} \phi_B^2 A \right)}{\frac{1}{K} \exp(K \phi_{A_1}) - \frac{1}{K} \exp(K \phi_{A_1}^o) - \ln \left(\frac{\phi_{A_1}}{\phi_{A_1}^o} \right) + \frac{r_{A_1} \phi_B}{r_B} - r_{A_1} \phi_B^2 B + \frac{\Delta H_{f,A}^o}{RT_{m,A}^o}} \quad (\text{S44})$$

References

1. C. M. Hansen, *Hansen's solubility Parameters: A Users Handbook*, CRC Press, Boca Raton, FL, 2007.
2. J. F. Toro-Vazquez, J. Morales-Rueda, A. Torres-Martinez, M. A. Charo-Alonso, V. A. Mallia and R. G. Weiss, *Langmuir*, 2013, **29**, 7642-7654.
3. K. A. Cavicchi, M. Pantoja and T.-Y. Lai, *ACS Symp. Ser.*, 2018, **1296**, 246-265.
4. P. J. Flory, *J Chem Phys*, 1944, **12**, 425-438.

5. J. William E. Acree, *Thermodynamic Properties of Nonelectrolyte Solutions*, Academic Press, Orlando, FL, 1984.
6. P. Painter, B. Veytsman and J. Youtcheff, *Energy & Fuels*, 2014, **28**, 2472-2480.
7. P. Painter, B. Veytsman and J. Youtcheff, *Energy & Fuels*, 2015, **29**, 2120-2133.
8. I. Prigogine, A. Bellemans and M. Mathot, *The Molecular Theory of Solutions*, Interscience Publishers, Inc., New York NY, 1957.