**Modeling Phase Transitions in DSC Experiments**

Dynamic Model Description

We have built a model to recreate the heat capacity curves in the DSC experiments, by explicitly tracking the transfer of material between the solid, liquid, and vapor phases. Currently, the model is based on thermodynamic properties of the pure components (i.e. vapor pressures, enthalpies of melting, etc), but mixture properties will be incorporated as well. The model ignores heat transport (i.e. energy is dispersed in the system instantaneously).

Using the experimental heat flow into or out of the system, the model predicts the flux of each species between each phase and the resulting temperature response. With this approach, the model recreates the temperature trends with mixed results depending on the concentration of water. In other words, the model can be tuned (typically the pure component heat capacities) to recreate well temperature trends for one trial, but then fails to the capture behavior of the other trials. This is likely due to unrealistic representation of heat absorbed by the solid phase.

The model so far has been able to corroborate the assumption that evaporation is negligible, but has not yet been able to reproduce the solid-liquid transitions seen in the experimental heat capacity trends. Our goal is to use the experimental data to fit the heat capacity and enthalpies of melting of the solids formed in the samples.

Vapor-Liquid Transitions

We have determined from a simple set of calculations (see Equilibrium Model description below) as well as through runs with the detailed model that no significant evaporation at all is expected in the system, consistent with the mass measurements. As a result, these interactions are not sufficient to reproduce any of the peaks in the experimental heat capacity trends. This includes the supposed “water boiling” peak apparent in the trends at 100 ᵒC (It is also clear from the amount of energy input to the system during those events that there is not enough energy to evaporate all of the water in the system). Probably this is condensed-phase interaction event as well.

Liquid-Liquid Interactions

Interactions within the liquid phase are calculated online with AIOMFAC. We do not yet simulate the presence of a separate organic phase, but instead just one mixed liquid phase. Thus, as the water concentration increases, the model predicts larger effects on the vapor pressures and solubilities of the organics than likely occurred in the real experimental systems. AIOMFAC predicts activity coefficients near 1 for most of the organic compounds even with 95 mol% water, except for dodecanoic acid, which has a strong predicted activity coefficient (~2000). This supports the inclusion of a separate liquid phase in the model, but the effects on the heat capacity predictions are uncertain.

Solid-Phase Transitions

The model treats solid-liquid and solid-gas transitions but these interactions require more development and testing. Currently, the model ignores diffusion within the liquid phase. It is not clear if this, in addition to the fast heat transport assumption, is reliable for simulating the melting case.



Equilibrium Calculation

We performed a simple partitioning calculation with pure-component vapor pressures (assuming that mixing effects would act to lower vapor pressure further) to predict whether or not significant evaporation would even be expected in this system. Table 1 demonstrates the strong driving force towards the condensed phase just from a straight-forward ideal partitioning argument. This analysis agrees with the observation of zero net mass loss from the DSC throughout the experiment.

**Table 1.** Pure Component Condensed Mass Fraction:

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **Vapor Pressure (atm)** | **Liquid Mass**  **(mg)** | **Liquid Vol.**  **(cm3)** | **Mass Concentration (mg m-3)\*** | **Condensed Mass Fraction** |
| Malonic Acid | 6.61E-09 | 0.72 | 4.42E-04 | 8.89E+06 | 0.99 |
| Succinic Acid | 3.1E-09 | 0.81 | 5.20E-04 | 1.01E+07 | 1.00 |
| Glutaric Acid | 1.73E-09 | 0.91 | 6.36E-04 | 1.13E+07 | 0.99 |
| Adipic Acid | 9.7E-10 | 1.00 | 7.39E-04 | 1.25E+07 | 0.99 |
| Pimelic Acid | 5.51E-10 | 1.10 | 8.59E-04 | 1.37E+07 | 0.99 |
| Suberic Acid | 3.15E-10 | 1.20 | 9.41E-04 | 1.49E+07 | 0.99 |
| Azelaic Acid | 1.81E-10 | 1.29 | 1.26E-03 | 1.61E+07 | 0.99 |
| Sebacic Acid | 1.05E-10 | 1.39 | 1.15E-03 | 1.73E+07 | 0.99 |
| Dodecanoic Acid | 1.72E-09 | 1.58 | 1.80E-03 | 1.96E+07 | 0.99 |
| Total |  | 10.00 | 8.05E-03 | 1.24E+08 | 1.00 |

\*Assume cell volume is approximately 10x larger than liquid volume

**Data and Calculations of Equilibrium for Cappa Mixture**

Physical Properties of Mixture:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Compound** | **MW**  **(g mol-1)** | **Enthalpy (kJ mol-1)a** | **Vapor Pressure (atm)** | **Density**  **(g cm-3)** | **Mole Fraction** | **Mass Fraction** |
| Malonic Acid | 104.06 | 141.9 | 6.61E-09 | 1.619 | 0.111 | 0.0715 |
| Succinic Acid | 118.09 | 88.5 | 3.1E-09 | 1.56 | 0.111 | 0.0812 |
| Glutaric Acid | 132.11 | 141.0 | 1.73E-09 | 1.429 | 0.111 | 0.0908 |
| Adipic Acid | 146.14 | 111.0 | 9.7E-10 | 1.36 | 0.111 | 0.1005 |
| Pimelic Acid | 160 | 124.0 | 5.51E-10 | 1.28 | 0.111 | 0.1100 |
| Suberic Acid | 174 | 130.0 | 3.15E-10 | 1.272 | 0.111 | 0.1196 |
| Azelaic Acid | 188 | 146.0 | 1.81E-10 | 1.0287 | 0.111 | 0.1293 |
| Sebacic Acid | 202 | 140.0 | 1.05E-10 | 1.209 | 0.111 | 0.1389 |
| Dodecanoic Acid | 230 | 119.0 | 1.72E-09 | 0.88 | 0.111 | 0.1581 |
| Total | 161.44b |  |  | 1.242c |  |  |

aCappa et al. (2008)

bMole-weighted

cMass-weighted

Pure component saturation concentration calculation:

Saturation Concentration **(mg m-3)** as a function of temperature:

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **T (deg C)** | **5** | **20** | **70** | **100** | **120** |
| Malonic Acid | 3.34E-04 | 7.34E-03 | 3.06E+01 | 1.54E+03 | 1.50E+04 |
| Succinic Acid | 9.69E-04 | 6.53E-03 | 1.11E+00 | 1.24E+01 | 5.03E+01 |
| Glutaric Acid | 1.14E-04 | 2.45E-03 | 9.68E+00 | 4.75E+02 | 4.56E+03 |
| Adipic Acid | 1.83E-04 | 2.03E-03 | 1.33E+00 | 2.81E+01 | 1.65E+02 |
| Pimelic Acid | 7.55E-05 | 1.12E-03 | 1.59E+00 | 4.84E+01 | 3.51E+02 |
| Suberic Acid | 3.88E-05 | 6.56E-04 | 1.34E+00 | 4.82E+01 | 3.86E+02 |
| Azelaic Acid | 1.45E-05 | 3.50E-04 | 1.86E+00 | 1.05E+02 | 1.10E+03 |
| Sebacic Acid | 1.09E-05 | 2.31E-04 | 8.56E-01 | 4.08E+01 | 3.86E+02 |
| Dodecanoic Acid | 3.97E-04 | 5.25E-03 | 5.55E+00 | 1.46E+02 | 9.80E+02 |