**Modeling DSC Experiments**

Dynamic Model

We have simulated the evolution of the organic/water DSC experiments with a system of prognostic equations describing the concentrations of the bulk and vapor masses as well as the temperature. The model explicitly represents mass transfer from the condensed to the vapor phase but does not represent solid-liquid transitions of any kind. Input for the model includes physical properties of the constituents and the experimental heating rate. The physical

We have found the model able to reproduce the temperature profile from the experiments, but unable to reproduce the heat capacity trends (Fig. 1). One possible explanation is that the model is missing the solid-liquid transitions that the experimental bulk heat capacity trend detects, thus supporting the experimental hypothesis. However, for this work we have assumed liquid heat capacity values that are constant with temperature and increase linearly with carbon number. This is somewhat guesswork, and we are interested in determining more realistic heat capacity values with the aid of SAR. Another interesting study will be to add a solid phase along with melting enthalpy to try to fit the energy of this phase transition to the experimental results.



**Figure 1.** Temperature and heat capacity in the DSC for the CappaMix without water. The features of the heat capacity trend are not reproduced by the model.

Equilibrium Calculation

Noting these issues, 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 |