Supporting Information

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SI Text

Temperature-Programmed Desorption (TPD) of Multicomponent Mixtures. The TPD method, as performed in our laboratory, has been described in detail (1, 2). In brief, polydisperse aerosols were produced by atomizing either methanol or aqueous solutions of the dicarboxylic acids with equimolar concentrations. For the mixtures, no differences in the TPD desorption profiles were observed whether water or methanol was used as the solvent. Here, either 9-component purely organic mixtures, comprising the C_3-C_{10} and C_{12} straight-chain dicarboylic acids [$(HOOC(CH_2)_nCOOH$, $C_x = C_{n+2}$] or mixed organic/inorganic mixtures were considered. The names of the diacids used are listed in supporting information (SI) Table S1. For the organic/inorganic mixtures, the same 9 diacids were used in equimolar amounts, but the total organic/inorganic molar ratio was 1:1. $NaNO_3$ was used as a representative inorganic component. The aerosols were dried by passing them through a horizontal flow tube partially filled with a 13X molecular sieve with a residence time of ≈3 min. The aerosols were introduced into the desorption chamber through a 30-cm-long, 0.25-mm-i.d. capillary inlet. The inlet collimated the aerosols into a well-defined beam. The aerosol beam was directed at the center of a circular flat-plate collector located <1 mm from the capillary exit. The collected aerosol was visible as a small mound with a shape that resembled a spherical cap with a base diameter (*d*) and height (*h*) that ranged from ≈0.2 to 0.6 mm. For each experiment an image of the sample was collected so that *d* and *h* could be determined via reference to the collector diameter (6.65 mm).

The temperature of the collected sample was linearly increased (≈0.02 K/s) and the evaporation rate for each compound was individually determined by using proton transfer reaction mass spectrometry (PTR-MS) (3). Although many of the compounds considered in this study fragment on ionization in the PTR-MS, for all of the compounds considered, at least one *m*/*z* was identified where the observed signal was dominated by, and therefore unique to, a single compound. The specific marker ions used are reported in Table S1. In all cases the contribution of the primary species at a given *m*/*z* was >80% of the total signal at that *m*/*z*, and for 5 of the 9 compounds it was 100%.

For this study, we have also measured the vapor pressure of pure malonic acid by using the same methods as detailed in ref. 1. The measured values of $p_s^0(298\text{ K})$, ΔH_{sub}, and ΔS_{sub} for the pure C_3 diacid were determined to be 2.2 (±0.5) × 10^{-4} Pa, 132.1 ± 5 $kJ \cdot mol^{-1}$, and 277.0 ± 16 $J \cdot mol^{-1} \cdot K^{-1}$, respectively.

Multicomponent Evaporation Model: Single Phase. The observed individual desorption profiles were interpreted by using a multicomponent evaporation model, based on a single-component model that accurately reproduces the desorption of pure dicarboxylic acids (*1*). The $p_{eff}^0(T)$ and evaporation rates of each component of the mixture were specified by their respective ΔH_{vap} and ΔS_{vap} through the relationship $\ln p_{eff}^0(T) = -\Delta H_{vap}/RT + \Delta S_{vap}/R$. The model was initialized assuming that the sample has a cylindrical shape containing N_{tot} molecules. Nearly identical results are obtained if we instead use a cone or half-sphere for the shape, the reasons for which have been previously discussed (1). The value of N_{tot} was determined directly from the observed signals and verified by comparison with the observed sample dimensions assuming an average density. The sample was assumed to be well-mixed such that the bulk and surface mole fractions are equal. At every time step, the number of molecules of compound *i* lost was determined from the pure component evaporation rate ($\sqrt{2\pi mkT}$) and the compound mole fraction (x_i) such that

$$N_{i,t} = N_{i,t-1} - x_{i,t-1} \cdot E_{i,t-1} \cdot SA_{t-1} \cdot \delta t, \qquad \textbf{[S1]}$$

where *SA* is the sample surface area (m^2). The total number of molecules remaining was

$$N_t = \sum_i N_{i,t}. \qquad \textbf{[S2]}$$

The x_i values were recalculated at every time step as

$$x_{i,t} = \frac{N_{i,t}}{N_t}. \qquad \textbf{[S3]}$$

One difference from our previous analysis is that we no longer assume that the volume change at every time step resulted from simultaneous equivalent decreases in both radius (*r*) and height (*h*), as observed for the pure solid samples (*1*). Instead, for the mixtures the height decreases faster than the radius such that $h_{t+1} = h_t \cdot f^{0.25}$, where *f* is the fraction of material remaining compared with the previous time step ($f = 1 - E_t \cdot \Delta t/N_t$). The empirical scaling factor (0.25) was chosen to provide for reasonable agreement between the model and the visual observations. In contrast to our studies on the pure compounds, we also found that it was unnecessary to "preheat" the 9-component mixtures to drive off residual solvent molecules (either water or methanol) before each TPD measurement (*1*), likely because of their liquid-like nature.

Thermodynamic parameters [ΔH_{vap}, ΔS_{vap}, and $p_{eff}^0(T)$] were derived by comparison with the model results and are compared with the values previously measured for the pure solid diacids (1) and also with their corresponding liquid-phase parameters at the same temperature (Table S2). The liquid vapor pressures (p_L^0) were determined from the measured solid values according to Eq. **4**.

$$\ln p_L^0(T) = \ln p_s^0(T) + \left[\frac{\Delta S_{fus}(T_m)}{R} \left(\frac{T_m}{T} - 1 \right) \right]. \qquad \textbf{[S4]}$$

where ΔS_{fus} is the entropy of fusion and T_m is the melting temperature (5, 6). Values for ΔS_{fus} and T_m are given in Table S1. A plot of $p_L^0(T)$ vs. $1/RT$ yields the liquid-phase ΔH_{vap} (slope) and ΔS_{vap} (intercept).

In this work all of the pure compound thermodynamics are for the liquid state, rather than the solid state. This has been done for two reasons: first, because it seems appropriate to compare with the liquid-phase thermodynamics in light of the observed liquid-like behavior, and second, because the observed ΔH_{vap} values are in generally good agreement with the pure compound liquid-state ΔH_{vap} (average deviation of 4%), whereas the solid-phase ΔH_{sub} are on average 25% greater. We also note that the use of mass fraction instead of mole fraction for Raoult's Law (7) has only a small influence on the vapor pressures, tending to increase the observed vapor pressures of the smallest diacids slightly and decrease the vapor pressures of the largest diacids. However, the deviations from ideality remain apparent.

To obtain quantitative agreement with the measurements we found that it was necessary to adjust the temperature-dependent liquid vapor pressures in the model from their pure liquid values. This was done by adjusting the enthalpy (ΔH_{vap}) and entropy (ΔS_{vap}) of vaporization from those of the pure component, where

$p^0_{\mathrm{eff}}(T) = -\Delta H_{\mathrm{vap}}/RT + \Delta S_{\mathrm{vap}}/R$ until a reasonable match between the observations and the model was obtained (Table S2). In general, the observed desorption profile for each component could be fit well by using a temperature-independent ΔH_{vap}, each of which was within 13% (average = 4%) of the estimated pure liquid-phase value.

Multicomponent Evaporation Model: Multiphase. We have investigated the possibility that our mixture was not "liquid-like" throughout the entire sample, but instead contained distinct solid and liquid organic phases, with the liquid phase being a nonaqueous solution of the diacids in equilibrium with the solid phase (i.e., a "nonaqueous phase liquid"). Note that a subcooled liquid is a special case of a nonaqueous phase liquid where the melting point depression for each compound is sufficient such that no solid phase exists. In a nonaqueous phase liquid, the liquid-phase composition is controlled by the requirement that the fugacities of the individual components in the solid and liquid phases be equal (8):

$$x_i^L \leq \frac{1\ f_i^s}{\gamma_i^L\ f_i^L} \qquad \textbf{[S5]}$$

where x_i^L is the liquid-phase mole fraction and f_i^x is the fugacity of compound i. The ratio f_i^s/f_i^L is approximately equal to p_i^s/f_i^L and thus can be estimated from Eq. **1**. Considering both Eqs. **1** and **3**, and assuming that $\gamma_i^L = 1$, we find that, in the absence of supercooling, no distinct liquid phase should be observed until $T \approx 318$ K for the 9-component diacid mixture used in this study. However, we observe the liquid-like behavior to begin by at least 300 K (Fig. 1*A*). If the values of γ_i^L shown in Fig. 2 are used instead, then a liquid phase is predicted to exist whenever $T > 284$ K, seemingly consistent with our observations.

If the system were a nonaqueous phase liquid (with distinct solid and liquid phases in equilibrium), evaporation would occur from both the solid and liquid phases with their relative importance being determined by the vapor pressures and mole fractions of the respective phases. To determine whether this interpretation is consistent with the observations, we have therefore adapted the TPD model to allow for simultaneous evaporation from solid and liquid phases, as would be the case if the samples were behaving as a nonaqueous phase liquid (NAPL; 8). Here, the saturation concentration (i.e., maximum mole fraction) of each compound that could theoretically exist in the NAPL at each temperature ($x_{i,\mathrm{NAPL}}$) was first calculated from Eqs. **1** and **3** in the main text. Initially it was assumed that $\gamma_i = 1$ for each of the compounds. This $x_{i,\mathrm{NAPL}}$ was compared with the total mole fraction for each compound ($x_{i,\mathrm{Total}}$). If $x_{i,\mathrm{NAPL}} > x_{i,\mathrm{Total}}$ then all of compound i was assumed to exist in the liquid phase. However, if $x_{i,\mathrm{NAPL}} < x_{i,\mathrm{Total}}$ then only $x_{i,\mathrm{NAPL}}$ was in the liquid phase and ($x_{i,\mathrm{Total}} - x_{i,\mathrm{NAPL}}$) remained in the solid phase. A further temperature-dependent constraint was applied wherein a liquid phase only existed when $\Sigma\, x_{i,\mathrm{NAPL}} \geq 1$; otherwise the sample was assumed to be a solid. The molecules that existed in the solid phase were assumed to have p_s^0 whereas those in the liquid phase were assumed to have p_L^0. An average p^0 was used for each compound, where $p^0 = p_L^0 \cdot x_{i,NAPL} + p_s^0 \cdot (x_{i,\mathrm{Total}} - x_{i,\mathrm{NAPL}})$. A crucial assumption of the multiphase model is that the solid and liquid phases maintain equilibrium at all times.

As in the single-phase model, the adjustable parameters used to describe each compound in the liquid phase were the ΔH_{vap} and ΔS_{vap}. The solid properties were assumed to be unchanged from those of the pure compounds. As the ΔH_{vap} and ΔS_{vap} were adjusted from the pure compound values to obtain a quantitative match with the observations, γ_i values were calculated. The calculated γ_i's were then allowed to feedback into the calculation of $x_{i,\mathrm{NAPL}}$ (compare Eq. **S5**), and the calculation was repeated until a good match was found between the model and the observations. This ensures that there is self-consistency between the calculation of the γ_i and the $x_{i,\mathrm{NAPL}}$.

Because of the assumption of solid–liquid equilibrium at every time step, evaporation within the model occurs primarily from the liquid phase. This is because the p_L^0 tend to be much higher than the p_s^0 values and evaporation primarily occurs from the higher vapor pressure liquid phase. As such, the primary difference between the multiphase model and the single-phase model is the calculation of the liquid-phase mole fraction that leads to the Raoult's Law vapor pressure lowering. In the case of the single-phase model, the x_i values are determined explicitly from Eq. **S3**. In the multiphase model the global solid-liquid equilibrium condition determines the liquid-phase mole fraction for each compound. Despite this difference, the activity coefficients estimated from the multiphase model are within 12% on average of the values determined by using the single-phase, liquid-only model. Thus, our conclusions are robust regardless of whether the sample was fully liquid-like or a NAPL, within the constraints of the assumption of instantaneous equilibrium between solid and liquid phases.

However, because diffusion in the solid phase is slow compared with the timescale of our experiments, the assumption of instantaneous equilibrium between solid and liquid phases may not be justified. If this is true, and if distinct solid and liquid phases did exist in our system, then the evaporation rate would be controlled in part by mass transfer between the two phases, which would be primarily determined by the diffusion rate in the solid. In such a case, the model, which assumes complete and instantaneous mixing, would have been incapable of describing the observations. Thus, our observations are consistent with the sample having been a well-mixed liquid throughout and inconsistent with the sample having been a NAPL.

Fusion/Melting Experiments. The melting and freezing behavior of a macroscopic mixture of the 9 diacids (C_3–C_{12}) was examined to determine the likelihood of the samples being supercooled. Equimolar amounts ($\approx 3 \times 10^{-3}$ moles) of each of the diacids were initially ground and mixed together with a mortar and pestle. This powdered mixture was placed into a round-bottom flask that was subsequently evacuated to $< \approx 0.5$ torr while still at room temperature. The temperature was controlled by variable heating with a heating mantle and the temperature monitored with a K-type thermocouple external to the flask.

On the initial heating cycle, the sample was observed to slowly change from opaque to translucent and bubbled somewhat vigorously for a short period. This was likely because of gases being trapped in the solid samples. On cooling and reheating this bubbling was no longer observed. If the mixture components had retained their pure compound properties we would expect the sample to become completely liquid at 455 K, the melting temperature of succinic acid, the C_4 diacid. However, the sample was observed to become completely translucent (indicating it had melted in entirety) in the range 360–370 K. This demonstrates the influence of the melting point depression due to mixing and is generally consistent with theory (9). We note that this "melting point" was higher for the initial heating when the sample had only been mixed by grinding, but fairly constant for future heating cycles. This is likely the result of the sample being better mixed at the molecular level after melting/freezing than after grinding. Here, we use the term "melting point" loosely, as there was no single, well-defined transition temperature; melting appeared to be a semicontinuous process driven by the mixture being composed of components with different T_m. The observed final melting point range was in generally good agreement with that predicted based on ideal mixing.

On cooling from the fully liquid state, the sample was not observed to turn opaque at the "melting point." Instead, it could be readily cooled up to ≈40 K below the melting point before any phase transition was visibly evident. The amount of supercooling showed some dependence on the cooling rate, with larger supercoolings observed for faster cooling rates. However, this relationship was not systematically investigated because the sample was not actively cooled (the heat was simply removed or decreased). The sample had a white, waxy appearance when cooled back to room temperature after melting. As with the melting process described above, there was no well-defined freezing point.

For this macroscopic mixture, the liquid-like nature of the sample was not readily evident below ≈320 K, and only slowly became apparent as the temperature was increased. However, the TPD measurements suggest that the TPD samples behaved quite liquid-like at temperatures as low as ≈300 K (see Fig. 1*A*). We speculate here as to the reason for the difference between the macroscopic mixture and the samples used in the TPD experiments. We suspect that the difference results primarily from the TPD samples coming from deposition of aerosols generated by atomization of either methanol or water solutions. These aerosols will be compositionally extremely well mixed while already at room temperature, or colder, once impacted on the collection plate. This can be contrasted with the macroscopic sample that might be fully mixed at high temperatures when it is liquid, but as the temperature was dropped there may have been preferential crystallization of the different components dependent on their individual T_m values. As such, when the macroscopic samples are returned to room temperature they may no longer be well mixed. For the aerosol-deposited samples used in the TPD experiments, it may be possible that they can remain as supercooled liquids for longer periods of time (at least a few hours, as deduced from the experiment timescale). Nonetheless, these observations using macroscopic samples demonstrate that the 9-component mixtures can be easily supercooled.

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Table S1. The dicarboxylic acids studied and the marker ions used to monitor their evaporation

	Molecular weight	Marker ion (*m*/*z*)	Melting point, K	ΔS_{fus}, J/mol·K
Malonic acid (C3)	104	105 (30)	408	56.6
Succinic acid (C4)	118	101 (99)	455.2	74.7
Glutaric acid (C5)	132	115 (52)	363.9	58.0
Adipic acid (C6)	146	111 (41)	419	80.4
Pimelic acid (C7)	160	69 (11), 97 (13), 125 (25)	368.2	68.4
Suberic acid (C8)	174	157 (50), 175 (24)	413.2	101.2
Azaleic acid (C9)	188	171 (43), 189 (34)	372.4	81.6
Sebacic acid (C10)	202	185 (32), 203 (37)	403.9	116.4
Dodecanoic acid (C12)	230	213 (30), 231 (68)	400.3	124.2

Values in parentheses indicate the percent of the total signal for that compound (+/− 10%). We also report the melting point and entropy of fusion ($= \Delta H_{\mathrm{fus}}/T_m$) of the diacids (5, 6).

Table S2. The ΔH_{vap}, ΔS_{vap} for the pure compound subcooled liquids and for the 9-component mixture

	$\Delta H_{vap,obs}$, kJ/mol	$\Delta H_{vap,pure}$, kJ/mol	$\Delta S_{vap,obs}$, J/mol· K	$\Delta S_{vap,pure}$, J/mol· K
Malonic acid (C3)	103	108	192	216
Succinic acid (C4)	94	95	152	175
Glutaric acid (C5)	105	111	195	215
Adipic acid (C6)	108	111	191	203
Pimelic acid (C7)	113	124	205	236
Suberic acid (C8)	135	130	256	246
Azaleic acid (C9)	148	146	301	282
Sebacic acid (C10)	134	140	248	260
Dodecanoic acid (C12)	119	119	208	203