Evaporation Rates and Vapor Pressures of the Even-Numbered C_8–C_{18} Monocarboxylic Acids

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Temperature-dependent vapor pressures of the even-numbered alkanoic monoacids from C_8–C_{18} were measured using temperature-programmed desorption (TPD). In TPD, the evaporation rates from the samples are directly measured and the vapor pressures are subsequently determined from the Hertz–Knudsen equation. Our measurements indicate that the vapor pressures of the solid even-numbered alkanoic acids decrease monotonically with increasing carbon number by more than 6 orders of magnitude going from C_8 to C_{18}. The enthalpies of sublimation increase monotonically with carbon number, from ~110 to 205 kJ/mol. The liquid-phase vapor pressure was measured for oleic acid, a C_{18} alkenoic acid. Comparison to the estimated liquid-phase vapor pressure for the corresponding C_{18} alkanoic acid indicates that the liquid-phase vapor pressures of these two compounds are identical. Our measured solid-phase vapor pressures for the C_{14} and larger alkanoic acids are lower than in previous studies. We attribute these differences to the influence of residual solvent molecules on the previous measurements, which cause the measured vapor pressures to be too large.

Introduction

Gas-to-particle partitioning of atmospheric organic aerosols depends in part on the temperature-dependent saturation vapor pressures of the various compounds that comprise the aerosol.[1] Organic compounds with sufficiently low vapor pressures will partition to the particle phase, thereby contributing to the total particle mass and its properties. However, there exist limited experimental measurements of temperature-dependent vapor pressures for most of the low volatility compounds that are commonly found in atmospheric aerosols.

Organic aerosols are composed of hundreds, if not thousands, of compounds,[2,3] and it would certainly be technically challenging to carry out vapor pressure measurements for every one of these compounds. An alternative approach is to perform systematic measurements of classes of compounds to facilitate development of estimation methods that can be used to predict vapor pressures. Such estimations are particularly important for difficult-to-synthesize compounds.

Herein, we describe measurements of the temperature-dependent vapor pressures of solid even-numbered straight-chain alkanoic monocarboxylic acids from C_8 to C_{18}. These measurements quantitatively demonstrate the importance of carbon chain length to the vapor pressure and enthalpy of vaporization of the monoacids. Additionally, we have measured the vapor pressure for the liquid-phase C_{18} alkenoic monoacid, oleic acid. The properties of this liquid monoacid are quantitatively compared to those of the corresponding solid-phase C_{18} alkanoic monoacid, stearic acid.

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Experimental Section

Evaporation rates of the even-numbered straight-chained alkanoic monocarboxylic acids from C_8 to C_{18} and of oleic acid, an alkenoic C_{18} monoacid (9-octadecenonic acid), were measured using a temperature-programmed desorption (TPD) method. The common names of the monocarboxylic acids are given in Table 1. The TPD method has been described in detail previously.[4] Briefly, samples of the various monoacid were deposited on a temperature controllable stage via aerosol impaction. The aerosols were generated by atomizing 1–2 wt % methanol solutions containing the individual monoacids and were made using HPLC grade methanol (>99.9% purity). The aerosols were dried by passing them through a diffusion drier prior to deposition. During deposition, the stage was maintained at a temperature at which the evaporation rate was below the detection limit of the system. The stage temperature was linearly increased at 1.5–3.5 K/min, and the evaporating molecules were detected using proton-transfer reaction mass spectrometry (PT-RMS). For each of the monoacids, with the exception of octanoic acid, an individual TPD experiment consisted of heating the deposited sample while monitoring the gas-phase abundance with the PT-RMS until the sample was completely evaporated. For all of the monoacids considered, the melting point (T_m) was within the temperature range of the TPD measurement, and the samples therefore melted before all of the deposited material evaporated. This solid-to-liquid phase transition influenced the measured desorption profiles, and it was not possible to fit the entire curve with a single set of thermodynamic parameters. Therefore, the data were fit only over the temperature range where the sample remained solid, that is, up to T_m. The deposited solid monocarboxylic acid samples were cone-shaped, except for octanoic acid and oleic acid, which were of spherically capped shape. Cone-shaped samples were previously observed by us for solid dicarboxylic acids.[4]

TABLE 1: Measured Vapor Pressures, Enthalpies, and Entropies of Sublimation or Vaporization for the Monocarboxylic Acids at 298 K

	p_S^0 (298 K) (Pa)	ΔH_{sub}^0 (kJ/mol)	ΔS_{sub}^0 (J/mol·K)
octanoic acid[a] ($H_3C(CH_2)_6COOH$)	2.5 (±0.9) × 10^{-1}	113.3 ± 6	272.5 ± 19
decanoic (capric) acid[a] ($H_3C(CH_2)_8COOH$)	5.4 (±1.1) × 10^{-2}	129.6 ± 5	314.6 ± 15
dodecanoic (lauric) acid[a] ($H_3C(CH_2)_{10}COOH$)	2.3 (±0.5) × 10^{-3}	147.2 ± 4	347.2 ± 13
tetradecanoic (myristic) acid[a] ($H_3C(CH_2)_{12}COOH$)	7.0 (±2.7) × 10^{-5}	168.6 ± 9	390.0 ± 31
hexadecanoic (palmitic) acid[a] ($H_3C(CH_2)_{14}COOH$)	1.3 (±0.4) × 10^{-7}	193.8 ± 11	441.7 ± 36
octadecanoic (stearic) acid[a] ($H_3C(CH_2)_{16}COOH$)	9.5 (±3.5) × 10^{-8}	204.1 ± 9	454.2 ± 31
octadecenoic (oleic) acid[b] ($H_3C(CH_2)_8{=}(CH_2)_8COOH$)	1.9 (±0.9) × 10^{-6}	135.6 ± 3	248.9 ± 8

[a] Solid phase. [b] Liquid phase.

Unlike the other alkanoic monoacids, neither octanoic acid nor the alkenoic acid oleic acid is solid at room temperature. This complicated the measurement of their vapor pressures with the TPD method because they did not deposit well in our system using aerosol impaction even when the stage was held below their respective melting point ($T_{m,octanoic}$ = 290 K and $T_{m,oleic}$ = 286 K). To overcome this limitation, these compounds were deposited by placing a small liquid drop (~6 mm diameter) on the stage instead of by aerosol impaction. During the sample addition, the stage temperature was held above their melting points. The samples were shaped as spherical caps rather than as cones. The shape of the sample is important because it is necessary to know how the surface area of the sample changes during a TPD experiment to quantitatively determine evaporation rates from these measurements. The surface area variation can be readily characterized for each TPD experiment as long as the sample has a well-defined shape.[4] The octanoic acid sample was subsequently cooled until it froze and the evaporation rate dropped below the detection limit of our system ($E \approx 10^{11}$ molecules s^{-1}); the spherical cap shape was maintained upon freezing. Thus, the vapor pressure for solid octanoic acid was measured even though it was deposited as a liquid.

Unlike octanoic acid, the evaporation rate for solid oleic acid was well below the detection limit. Thus, the evaporation rate and vapor pressure were instead measured for liquid oleic acid. The amount of octanoic and oleic acid deposited was large as compared to the aerosol deposition method used for the other monoacids. Correspondingly, the surface area was large, and, as a result, the observed evaporation rates for these samples became sufficiently large to significantly deplete the H_3O^+ reagent ion as the sample was heated. Under normal operating conditions, $[H_3O^+] \gg [R]$ and the proton-transfer reaction can be treated as a pseudo first-order reaction (where R is the monoacid to be detected). However, when R becomes large the H_3O^+ ion is reacted away and the linear response of the system is lost. Therefore, the octanoic and oleic acid evaporation rates were only measured over a limited temperature range (ca. 240–270 K for octanoic acid and 305–340 K for oleic acid) instead of until the point where no sample remained so that at all times $H_3O^+ \gg R$. Over this temperature range, the amount of sample that evaporated was small as compared to the total sample amount and the surface area remained nearly constant during each TPD experiment. For reference, the detection limit corresponds to a vapor pressure of ~10^{-5} Pa for the solid samples generated by aerosol deposition but ~10^{-7} Pa for the liquid samples because of their much larger surface area.

Prior to each TPD experiment, the samples were "preheated" for 30–60 min (Table 2).[4] For octanoic acid (where there was no maximum), the preheating temperature was chosen to be 10 K above the melting point. For oleic acid, the preheating temperature was the same as for stearic acid. We have previously shown that preheating is crucial in accurately determining the

TABLE 2: Temperatures at Which the Samples Were Collected and "Preheated"[a]

	$T_{deposit}$ (K)	$T_{preheat}$ (K)
octanoic acid	230	278
decanoic acid	<245	283
dodecanoic acid	<250	300
tetradecanoic acid	<258	320
hexadecanoic acid	<263	330
octadecanoic acid	<273	341
oleic acid	<280	336

[a] The preheating temperatures varied by up to ±3 K between different experiments.

vapor pressures of the diacids; without preheating, residual solvent molecules from the aerosol atomization process had a strong influence on the measured vapor pressures.[4]

We have also performed experiments with stearic acid where the sample was "recycled" for use in subsequent TPD experiments. Here, an initial experiment was performed where the stearic acid sample had the typical cone shape. The stearic acid sample was heated and the evaporation rate measured until it melted and the sample changed shape from a cone to a spherical cap. Before the entire sample evaporated, it was cooled and a second TPD experiment was performed using the stearic acid sample with the now spherical cap shape. The same sample was recycled for use in two further TPD experiments. No significant difference was observed between the vapor pressures determined from the measurements using the cone-shaped samples and any of the spherical cap-shaped samples. This provides support for our treatment of the octanoic and oleic acid samples. This result also indicates that the influence of nonvolatile impurities, the fraction of which would increase with each recycled sample, on the measured properties is negligible.

Data Analysis

Vapor pressures of the individual monoacids were determined from the evaporation measurements in the same manner as the diacid vapor pressures.[4] In brief, the measured evaporation rates (molecules/s) at every temperature were converted to fluxes by dividing by the sample surface area. As was done previously, the surface area of the initially deposited samples was determined directly from visual inspection of the sample dimensions (base diameter and height). The variation of the surface area with temperature was determined from a model of evaporation that is based on the measured evaporation rate where it was assumed that the change in volume (due to evaporation mass loss) results from equivalent decreases in the cone base diameter and height. For octanoic acid and oleic acid, the samples were instead treated as half-spheres. However, we have previously demonstrated that the derived evaporation fluxes and vapor pressures are insensitive to the assumed sample shape to within 10%.[4]
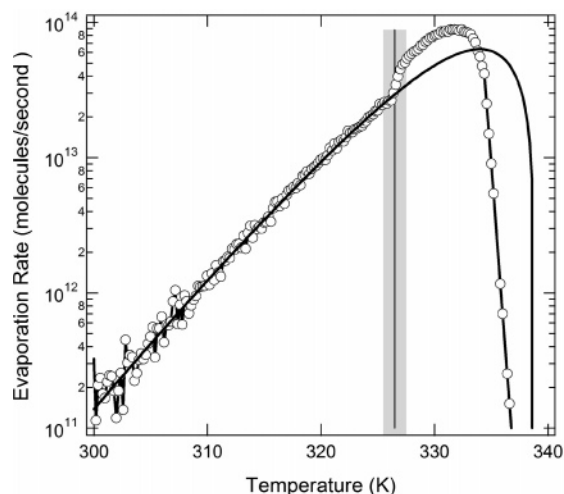
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Figure 1. The measured desorption profile for tetradecanoic acid (open symbols) as compared to the calculated profile (solid line). Note the *y*-axis is a log scale. The calculated profile was determined by fitting the data only below $T = 327$ K, the temperature at which the sample was observed to melt. The observed melting temperature is equal to the literature melting temperature (indicated as vertical black line shown with error bars in gray).[14] The simultaneous change in vapor pressure and surface area upon melting precludes determination of the liquid-phase properties from the measurements.

The temperature-dependent fluxes were converted to vapor pressures through use of the Hertz–Knudsen equation[5]

$$J_e(T) = \frac{E(T)}{SA(T)} = \frac{\gamma_e p^0(T)}{\sqrt{2\pi mkT}} \tag{1}$$

where p^0 is the vapor pressure (Pa), m is the molecular mass (kg/molecule), k is Boltzmann's constant (J/K), T is temperature (K), and SA is the surface area of the sample (m^2). γ_e is the so-called evaporation coefficient, and we make the generally accepted assumption that γ_e is unity.[6–8] This assumption means that the derived vapor pressures are therefore lower limits to the true vapor pressure. Even if γ_e is less than unity, the ΔH values derived here are still valid so long as γ_e is not strongly temperature dependent.

The TPD method provides a direct measure of the compound vapor pressure, within the constraints of the assumption that $\gamma_e = 1$. We have demonstrated previously that the uncertainty in the derived vapor pressures from use of the cone model for evaporation is typically smaller than the precision of the measurement. The reported uncertainties are therefore reported as two standard deviations determined from at least three independent measurements.

Over the limited temperature range of our experiments, a plot of $\ln p^0$ versus $1/T$ is linear with a slope equal to $\Delta H_{sub}^0/R$ and an intercept approximately equal to $\Delta S_{sub}^0/R$, where ΔH_{sub}^0 is the enthalpy of sublimation, ΔS_{sub}^0 is the entropy of sublimation, and R is the ideal-gas constant. For each of the compounds considered, the vapor pressures are reported at 298 K to facilitate comparison with previous measurements.

Results

An example of the desorption profile obtained from a TPD experiment using tetradecanoic acid, where the sample melting point was reached before the sample was completely evaporated, is shown in Figure 1. Once the sample melted, the observed evaporation rate increased both because the vapor pressure of the liquid was higher than that of the solid for $T > T_m$ and
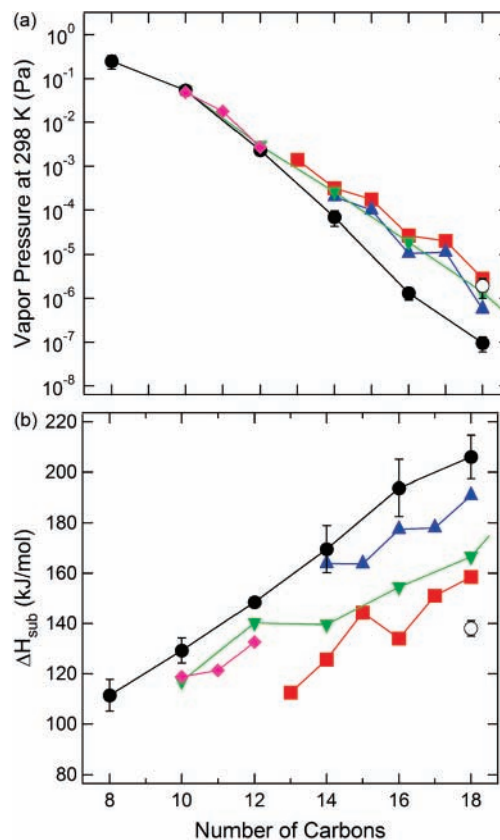

Figure 2. (a) Vapor pressures measured for the solid alkanoic monocarboxylic acids (●) and for liquid oleic acid (○). Vapor pressures measured by Chattopadhyay and Ziemann (■, red), Davies and Malpass (▼, green), Tao and McMurray (▲, blue), and Baccanari et al. (◆, pink) are shown for comparison. (b) Measured sublimation enthalpies (or vaporization for oleic acid) are shown. Symbols are the same as in (a).

because the surface area increased as the shape of the sample changed. It was not possible to simultaneously account for these two effects, and the thermodynamic parameters were therefore determined only for the solid sample, that is, for $T < T_m$. Similar desorption profiles were obtained for the other monoacids (excluding octanoic and oleic acid, as discussed above).

The vapor pressures and sublimation enthalpies measured for the even-numbered monoacids are shown in Figure 2 and reported in Table 1 along with the ΔH_{sub}^0 and ΔS_{sub}^0. (Note that for oleic acid the liquid-phase properties are reported, that is, the enthalpy and entropy of vaporization. Also, to facilitate comparison with the other alkanoic monoacids, the equivalent solid-phase properties are reported at 298 K for octanoic acid even though it is a liquid at 298 K.) The vapor pressures of the solid even-numbered alkanoic acids decrease monotonically with increasing carbon number. In going from C_8 to C_{18}, the vapor pressures decrease by more than 6 orders of magnitude. The ΔH_{vap}^0 and ΔS_{vap}^0 increase monotonically with carbon number. This general behavior is similar to that reported previously for these compounds.[9–12]

Discussion

The agreement between the vapor pressures of the solid monoacids measured in this study and in previous studies is excellent for the C_{10} and C_{12} monoacids.[9,11] However, the vapor pressures of the C_{14} and larger monoacids measured here are systematically lower than the previous measurements.[10–12] This difference increases with carbon number. The sublimation enthalpies measured here are all generally higher than the

TABLE 3: Vapor Pressures and Thermodynamic Parameters for the Liquid-Phase Alkanoic Acids Calculated Using the Measured Solid-Phase Vapor Pressures and Equation 2[a]

	p_L^0 (298 K) (Pa)	ΔH_{vap}^0 (kJ/mol)	ΔS_{vap}^0 (J/mol·K)	ΔS_m^b (J/mol·K)	T_m^b (K)
octanoic acid	$1.9\ (\pm 0.7) \times 10^{-1}$	91.9	198.7	73.8	289.7 ± 0.7
decanoic acid	$6.7\ (\pm 1.5) \times 10^{-2}$	101.8	223.3	91.3	304.6 ± 2
dodecanoic acid	$5.4\ (\pm 1.2) \times 10^{-3}$	111.8	232.7	114.5	317.0 ± 2
tetradecanoic acid	$3.4\ (\pm 1.5) \times 10^{-4}$	123.5	252.2	137.8	327.3 ± 1
hexadecanoic acid	$1.4\ (\pm 0.6) \times 10^{-5}$	140.1	281.6	160.0	335.7 ± 1
octadecanoic acid	$2.2\ (\pm 1.1) \times 10^{-6}$	143.1	276.1	178.1	342.5 ± 3

[a] The uncertainties in the p_L^0 were determined by propagating the errors in p_s^0, ΔS_m, and T_m. The uncertainty in ΔS_m was not given in the NIST database; we assumed a 1σ uncertainty of $\pm 5\%$. [b] From NIST Webbook.[14]

previous measurements. A similar discrepancy between the vapor pressures and sublimation enthalpies measured using our TPD method and other methods for the solid dicarboxylic acids has been observed.[4] In that study, the difference between our measurements and prior measurements was attributed primarily to the influence of residual solvent molecules on the measured vapor pressures. It was shown that the preheating step that is part of our TPD measurements serves to facilitate removal of any residual solvent. It is likely that a similar solvent removal effect is responsible for the differences observed for the monoacids in this work.

The vapor pressure of oleic acid at 298 K is significantly higher than that of stearic acid even though the two compounds have the same number of carbons. This difference is easily understood and results from oleic acid being a liquid and stearic acid being a solid in these measurements. Similarly, the measured ΔH_{vap}^0 for oleic acid is lower than ΔH_{sub}^0 for stearic acid. The vapor pressure of the solid phase is related to that of the liquid phase through the equation[13]

$$\ln p_L^0(T) = \ln p_s^0(T) + \left[\frac{\Delta S_m(T_m)}{R}\left(\frac{T_m}{T} - 1\right)\right] \quad (2)$$

where ΔS_m is the entropy of fusion and T_m is the melting temperature.[14] If we calculate the liquid-phase vapor pressure (at 298 K) for stearic acid using our measured p_s^0, we find that it is identical to that measured for liquid oleic acid. This is not surprising given their nearly identical structures. The calculated ΔH_{vap}^0 for liquid-phase stearic acid is also the same as that for liquid oleic acid. The excellent correspondence between oleic and stearic acid provides confidence in our measurements.

The liquid-phase properties of these and other low-volatility compounds are thought to be important in determining their gas-particle partitioning in atmospheric aerosols.[1] This is because atmospheric organic aerosol is a complex mixture of organics and this leads to liquid-like behavior due to the entropy of mixing. We have therefore also calculated the liquid-phase vapor pressures and enthalpies of vaporization at 298 K for the other alkanoic monoacids from eq 2 (Table 3, Figure 3) using known values of ΔS_m and T_m.[14] At 298 K, the liquid-phase vapor pressures are higher than the solid phase, with the exception of octanoic acid. For octanoic acid, the melting point is below 298 K, and therefore the liquid phase is the thermodynamically favored state. The liquid-phase vapor pressure is therefore slightly lower than for the corresponding overheated solid phase; we report the value at 298 K only for consistency with the other measurements. That the difference between the solid and liquid vapor pressures increases with carbon number is a consequence of the melting point increasing with carbon number; the correspondence between the liquid-phase and solid-phase vapor pressures depends on the selected reference temperature (here, 298 K). For all of the monoacids, ΔH_{vap}^0 is less than ΔH_{sub}^0
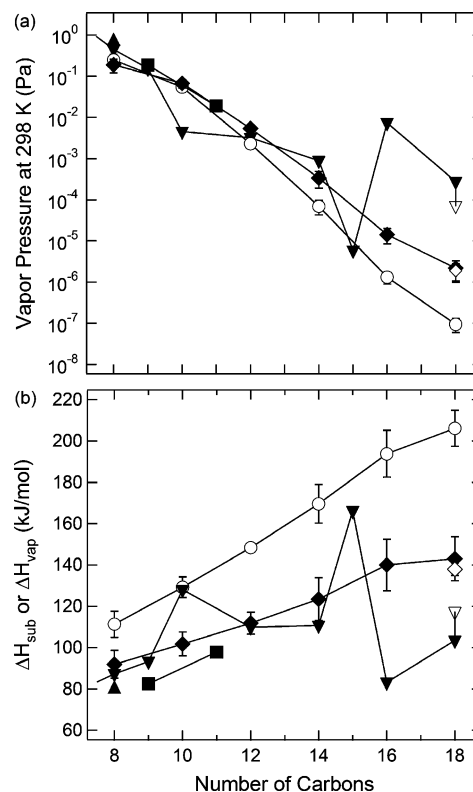
Figure 3. (a) Liquid-phase vapor pressures for the alkanoic acids (♦) and for oleic acid (◇) at 298 K estimated from the solid-phase vapor pressures and eq 2. Shown for comparison are the solid-phase properties (○) and the liquid-phase values from Yaws (▼, = alkanoic, ▽ = oleic acid), Baccanari et al. (■), and Verevkin et al. (▲). (b) Enthalpy of sublimation or vaporization for the alkanoic acids and oleic acid. Symbols are the same as in (a).

because $\Delta H_{vap}^0 = \Delta H_{sub}^0 - \Delta S_m \cdot T_m$. Our estimated liquid-phase vapor pressures show much less scatter than those reported by Yaws (Figure 3).[15] The large variability in the Yaws vapor pressures is unphysical. For compounds such as the monocarboxylic acids, we would expect the liquid-phase vapor pressures to decrease approximately monotonically with increasing carbon number. Our derived values are consistent with this expectation. Although we have not measured the vapor pressures for the odd-numbered alkanoic monocarboxylic acids, we can reasonably expect that their liquid-phase vapor pressures should lie linearly between the even-numbered monoacids. The vapor pressures of the solid monoacids would then be expected to show a weak "seesaw" pattern due to differences in the ΔS_{melt} and T_m between the even and odd-numbered monoacids, as has been observed in other experimental measurements of the monocarboxylic acid vapor pressures.[10,12]

The liquid-phase vapor pressures were also compared to calculated vapor pressures from various group contribution methods and from a boiling point-based method (Figure 4).
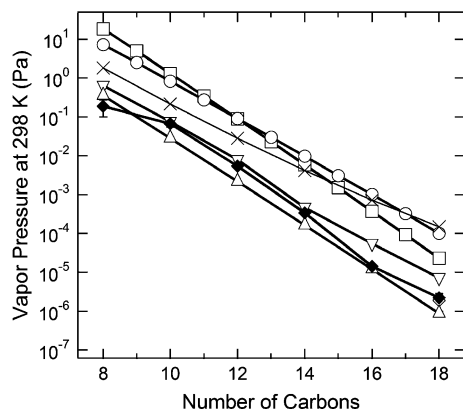
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Figure 4. Comparison between the estimated liquid-phase vapor pressures from our TPD measurements (◆) as compared to calculated vapor pressures using SPARC (▽), UNIFAC with parametrizations given by Jensen et al. (○), Asher et al. (□), and Asher and Pankow (△), and the Myrdal and Yalkowsky method (×) at 298 K.

Group contribution methods parametrize the total interaction between molecules in terms of the interactions between the constituent functional groups,[13] while the boiling point-based method utilizes an integrated form of the Clausius–Clapeyron equation along with known or estimated thermodynamic parameters (i.e., the Myrdal and Yalkowski method).[16,17] Vapor pressures calculated using the UNIFAC group-contribution method with parameters taken from Jensen et al. (1981) or Asher et al. (2002) are higher than our estimated liquid-phase vapor pressures by approximately an order of magnitude.[18,19] However, the vapor pressures calculated using the SPARC method or using the revised UNIFAC method with updated parameters as given in Asher and Pankow (2006) agree quite well with our measurements, in terms of both the absolute values and the decrease due to addition of –CH2 groups.[20–22] For the homologous straight-chain dicarboxylic acids, we previously found that the UNIFAC method of Asher et al. (2002) also predicted vapor pressures higher than the measured values.[4] However, we find that use of the revised UNIFAC method[20] does not lead to improved agreement with the measured dicarboxylic acids vapor pressures, in contrast to what was found for the monocarboxylic acids above. The reasons for this are unclear, but demonstrate the difficulties associated with developing robust group contribution methods for estimating vapor pressures of very low volatility compounds. We also find that vapor pressures predicted using the method of Myrdal and Yalkowsky are higher than those measured here and furthermore that the decrease in the vapor pressure upon addition of a CH2 subunit is too weak.

Considered in terms of partitioning theory,[1] use of the monocarboxylic acids vapor pressures measured here leads to more organic mass being calculated to be in the aerosol phase when compared to the UNIFAC method of either Jensen et al. (1981) or Asher et al. (2002) or to the Myrdal and Yalkowski method, in contrast to the SPARC or revised UNIFAC method. This will not be the case for the dicarboxylic acids[4] because, as noted above, the revised UNIFAC method does not agree with the experimental measurements. Attempts to quantitatively model organic aerosol formation both in the lab and in the atmosphere using chemical mechanisms of varying detail[23–25] will therefore depend importantly on the vapor pressure estimation method used and the chemical composition of the organic aerosol. Systematic measurements of vapor pressures of common organic aerosol components, such as those presented here, will facilitate further development of the parameters used in the various vapor pressure estimation methods. However, we caution about the direct use of these single component vapor pressures in the calculation of gas-particle partitioning in multicomponent aerosol systems because the activity coefficients of the various components may differ significantly from unity, consequently either raising or lowering the effective vapor pressures.[26] Additionally, particle-phase chemical reactions of the carboxylic acids with, for example, basic compounds may decrease the overall vapor pressure the system.

Conclusions

Vapor pressures of the solid even-numbered straight-chain alkanoic acids have been determined from evaporation rates measured using a temperature-programmed desorption technique. The measurements indicate that the solid-phase vapor pressures decrease monotonically with increasing carbon number while the enthalpy and entropy of sublimation increase with carbon number. The vapor pressures for the monoacids larger than C_{12} determined in this study are somewhat lower than those measured previously. We attribute this difference to the removal of solvent from the samples prior to the vapor pressure measurement by "preheating" the samples. This is consistent with results from our prior study on dicarboxylic acid vapor pressures.[4]

The liquid-phase vapor pressure of oleic acid, a C_{18} alkenoic acid, was also measured. Excellent agreement was found between the measured vapor pressure and ΔH_{vap} for oleic acid and the estimated liquid-phase vapor pressure and ΔH_{vap} for the C_{18} alkanoic acid, stearic acid. The estimated liquid-phase vapor pressures for all of the alkanoic acids were compared to theoretical predictions from group contribution methods. We found that the SPARC method and the UNIFAC method (using the updated parameters of Asher and Pankow (2006)) agreed well with the measurements, in contrast to the UNIFAC predictions when either the Jensen or the Asher et al. (2002) parametrizations were used. However, the better performance of the Asher and Pankow (2006) UNIFAC parametrization for the monocarboxylic acids does not carry over to predictions of diacids vapor pressures.[4]

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