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Adipic and Malonic Acid Aqueous Solutions: Surface Tensions and Saturation Vapor Pressures

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The surface tension of adipic aqueous solutions was measured as a function of temperature ($T = 278-313$ K) and adipic acid mole fraction ($X = 0.000-0.003$) using the Wilhelmy plate method. A parametrization fitted to these data is presented. The evaporation rates of binary water−malonic and water−adipic acid droplets were measured with a TDMA technique at different temperatures ($T = 293-300$ K) and relative humidities (58−80%), and the saturation vapor pressures of subcooled liquid malonic and adipic acids were derived from the data using a binary evaporation model. The temperature dependence of the vapor pressures was obtained as least-squares fits to the derived vapor pressures: $\ln(P_{\mathrm{sat,l}})$ (Pa) $= 220.2389 - 22634.96/T$ (K) $- 26.66767 \ln T$ (K) for malonic acid and $\ln(P_{\mathrm{sat,l}})$ (Pa) $= 140.6704 - 18230.97/T$ (K) $- 15.48011 \ln T$ (K) for adipic acid.

1. Introduction

Atmospheric aerosol particles have significant effects on life on Earth, particularly via their climatic importance,[1−3] negative impact on human health,[4,5] and ability to reduce visibility in densely populated areas.[6] The Intergovermental Panel on Climate Change (IPCC) stated in their latest report[7] that the largest uncertainties related to the scientific understanding of climate change are connected to atmospheric aerosols, although significant improvement has been made since the previous corresponding report from 2001.[8] Aerosol particles affect the Earth's radiation balance in two distinct ways. First, they directly scatter and absorb solar radiation, depending on their optical properties. Second, they act as condensation nuclei for cloud droplets (CCN), therefore affecting the properties of the atmospheric cloud cover. To understand the climatic effects of atmospheric aerosols, features of their formation and growth mechanisms, composition, as well as their ability to act as cloud condensation nuclei need to be quantitatively known.

Organics have been identified as important constituents of the atmospheric particulate matter,[9−11] especially over continental regions. Recent studies[12−15] suggest that organic compounds are likely to have a crucial role in the formation and growth of atmospheric aerosol particles, as well as in affecting their potential to act as CCN.[16−20] On the other hand, the knowledge as to the properties of atmospherically relevant organics is still rather poor; although significant progress has been made during the recent years.[11]

Knowledge on the thermophysical properties of atmospheric organics is crucial for modeling their role in gas−aerosol partitioning and aerosol−cloud interactions.[11,21] Information on the surface tensions and densities of the atmospheric organic mixtures, as well as condensed-phase activities and saturation vapor pressures, are of particular importance. Surface tensions and densities govern the Kelvin effect and are therefore particularly important in nucleation and cloud droplet activation studies, whereas the saturation vapor pressures and condensed-phase activities govern all processes involving phase transitions. Studies on the binary aqueous solutions are the first steps toward atmospherically relevant mixtures but are often needed to accurately model the multicomponent mixtures.

Aliphatic straight-chain dicarboxylic acids such as malonic, succinic, glutaric, and adipic acids are water soluble organic acids that are commonly found in atmospheric aerosol samples.[22−25] This implies that they partition to the condensed phase and therefore affect the formation and growth as well as the cloud droplet activation properties of aerosol. To understand these effects, information on the thermophysical properties of these acids is required. Malonic, succinic, glutaric, and adipic acids have a general formula of $\mathrm{HOOC(CH)}_n\mathrm{COOH}$ and are often referred to according to their carbon number (C3, C4, C5, and C6, respectively). All the pure acids are solid under atmospheric conditions, but as theoretically shown by Marcolli et al.,[26] as the molecules are mixed in the particle phase, the liquid state could be the thermodynamically stable phase in atmospheric conditions.

During recent years, a notable effort has been made to understand the properties of C3−C6 dicarboxylic acids. Hyvärinen et al.[27] reported the surface tensions of binary aqueous solutions containing C3−C5 dicarboxylic acids. Topping et al.[28] presented measured and modeled surface tensions of multicom-

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ponent aqueous solutions containing dicarboxylic acids. Topping et al.[28] also emphasized that to accurately model the ternary systems including inorganic compounds, information on the behavior of binary aqueous systems is required (see also Henning et al.[19]). Roux et al.[29] recently measured vaporization, fusion, and sublimation enthalpies of dicarboxylic acids using differential scanning calorimetry. Solid-state vapor pressures of these acids have been derived by Tao and McMurry,[30] Bilde and Pandis,[31] and Bilde et al.[32] using a TDMA system; by Ribeiro da Silva et al.[33] with effusion methods; and most recently by Chattopadhyay and Ziemann[34] and Cappa et al.[35] with temperature programmed thermal desorption methods. The magnitudes of the reported vapor pressures are relatively low (10^{-6} −to 10^{-3} Pa, varying significantly between different studies), suggesting that the acids may contribute to secondary aerosol formation. Peng et al.[36] studied the hygroscopic growth of dicarboxylic acid aerosols and obtained information on the water activities in binary aqueous solutions of these acids. Clegg and Seinfeld[37,38] on the other hand, developed comprehensive thermodynamic models for multicomponent solutions including organic acids and inorganic salts.

Recently, Riipinen et al.[39] and Koponen et al.[40] presented a method to determine the liquid-phase vapor pressures of the dicarboxylic acids and reported saturation vapor pressures for the subcooled malonic, succinic, and glutaric (C3−C5) acids. The method was based on measuring the evaporation rates of aqueous acid solution droplets and modeling the evaporation with an accurate binary condensation model.[41] In these studies, however, temperature-dependent expressions were reported only for succinic (C4) and glutaric (C5) acids. Zardini et al.[42] recently determined the temperature-dependent subcooled liquid saturation vapor pressure for malonic (C3) acid by detecting the evaporation rates of aqueous malonic acid solution droplets with an optical method.

Even though a reasonable amount of data are nowadays available for the C3−C6 dicarboxylic acids aqueous solutions, to our knowledge, measurements on the adipic acid (C6) mixture surface tension and liquid saturation vapor pressures are still missing. In this work, we present such data, following the approaches presented in Hyvärinen et al.,[27] Riipinen et al.,[39] and Koponen et al..[40] We also present more data on the subcooled liquid vapor pressure of malonic acid (C3), as data points in only two temperatures were presented by Koponen et al.[40] The main purpose of this work is to complete the data sets on the surface tensions of the aqueous solutions and subcooled liquid vapor pressures of the C3−C6 dicarboxylic acids, expressed as a function of acid mole fraction (surface tension) and temperature (surface tension and vapor pressure).

2. Materials and Methods

2.1. Experiments. *2.1.1. Surface Tension Measurements for Adipic Acid Aqueous Solution.* The surface tensions of binary mixtures of water and adipic acid were measured with a thermostated tensiometer (Digital Tensiometer K 10ST, Krüss, Gmbh,) using the Wilhelmy plate method.[43] The surface tension measurements were conducted at 18 different compositions, the adipic acid solubility (∼0.003 mole fraction[26,44]) setting the upper limit for the studied concentration range. The temperature was controlled with a circulation liquid bath (Lauda RC6 CS). Adipic acid was provided as >99.5% purity solid (Fluka) and was dissolved in purified water (Milli-Q, 18 M).

The preparation of samples and the actual surface tension measurements were made in a similar way as described by Hyvärinen et al.[27] The surface tension measurements were made with an estimated uncertainty of less than 1.0%, at temperatures from approximately 278 to 313 K.

2.1.2. Evaporation Rates of Adipic and Malonic Acid Aqueous Solutions. The evaporation rates of binary droplets containing water and adipic or malonic acid were measured using the Tandem-DMA technique[45] modified to study aqueous solution droplets. Droplets were generated by atomizing aqueous solutions of adipic and malonic acids, and an almost monodisperse size fraction was selected with a DMA. The selected droplets were allowed to evaporate in a laminar flow tube during a well-defined time, and the decrease in particle size was monitored with a second DMA. Temperature and relative humidity were controlled throughout the experimental system. For detailed descriptions of the measurement setup, see Bilde et al.,[32] Mønster et al.,[46] and Koponen et al.[40] Adipic and malonic acids were obtained as >99.5 and >99% purity solids (Fluka) and were dissolved in double deionized water purified with a Milli-Q Plus Ultrapure water system. The experiments were repeated for eight and nine different temperatures and relative humidities for malonic and adipic acids, respectively. The investigated temperatures ranged from 293 to 300 K, and the relative humidities were 58−75% for malonic acid and 59−80% for adipic acid. Peng et al.[36] measured the hygrospcopicity of C3−C5 diacids and observed no clear deliquescence or crystallization points for malonic acid, suggesting that it stays in saturated aqueous solution in all of the studied RHs. Unfortunately, such measurements do not exist for adipic acid, and this cannot be ignored. However, we can assume that the crystallization of adipic acid is likely to happen at RHs close to the succinic and glutaric acid values (29−59%). Also, in our measurements, we did not see any indication of crystallization behavior of adipic acid, suggesting that also the adipic acid aerosols are in the phase of an aqueous solution. The aerosol flow rates in the laminar flow tube were 0.3 or 1 L/min, the corresponding sheath flow rates being 0.6 and 2.0 L/min. The droplet concentrations were also varied to test the possible effect of increasing gas-phase concentrations of the acids. To test for reproducibility, the droplet diameter was measured at least twice at each sampling port within a time interval of tens of minutes to hours.

2.2. Data Evaluation. *2.2.1. Parametrization for the Surface Tension of Adipic Acid Aqueous Solution.* The surface tension of the adipic acid aqueous solution was parametrized by fitting an expression of the form[27,47]

$$\sigma_{\mathrm{mix}} = (1-X)\sigma_1 + X\sigma_2 - R_{\mathrm{m}}TX(1-X)\left[\frac{1}{\Lambda_{12}X + (1-X)} \times \left(\frac{\partial \Lambda_{12}}{\partial A}\right) + \frac{1}{\Lambda_{21}(1-X) + X}\left(\frac{\partial \Lambda_{21}}{\partial A}\right)\right] \quad (1)$$

to the measured surface tensions, where

$$\Lambda_{ij} = \exp\left(-\frac{U_{ij} - U_{ii}}{R_{\mathrm{m}}T}\right) \quad (2)$$

and

$$\left(\frac{\partial \Lambda_{ij}}{\partial A}\right) = -\frac{\Lambda_{ij}}{RT}\left(\frac{\partial (U_{ij} - U_{ii})}{\partial A}\right)_{T,P,X} (i, j = 1, 2) \quad (3)$$

The variables $U_{12} - U_{11}$, $U_{21} - U_{22}$, $(\partial(U_{12} - U_{11})/\partial A)_{T,P,X}$, and $(\partial(U_{21} - U_{22})/\partial A)_{T,P,X}$ were used as the fitting parameters. In eqs 1−3, the subscript 1 refers to water and 2 to adipic acid, X is the adipic acid mole fraction, σ_{mix} refers to the mixture surface tension (mN/m), and σ_{i} is the surface tension of pure

TABLE 1: Measured Surface Tension (σ) of Adipic Acid Aqueous Solution for Different Adipic Acid Mole Fractions (X) at 298 K

X	σ (mN/m)
0.00005	71.0
0.00009	71.1
0.00010	70.7
0.00030	70.0
0.00050	69.6
0.00060	69.3
0.00080	68.3
0.00090	68.1
0.00130	67.4
0.00150	66.7
0.00180	66.4
0.00180	66.1
0.0020	65.4
0.00220	65.5
0.00220	65.0
0.00250	64.7
0.00260	64.7
0.00280	64.6

TABLE 2: Measured Surface Tension (σ) of Adipic Acid Aqueous Solution as a Function of Temperature (T)

$X = \sim 0.0006$		$X = \sim 0.001$		$X = \sim 0.0015$		$X = \sim 0.0018$	
T (K)	σ (mN/m)	T (K)	σ (mN/m)	T (K)	σ (mN/m)	T (K)	σ (mN/m)
280.9	71.1	280.1	69.6	282.4	68.2	279.6	67.6
285.3	70.5	281.9	69.3	284.2	68.1	285.8	66.5
286.3	70.6	284.3	69.4	286.2	67.9	289.8	66.6
288.3	69.7	285.2	69.2	287.7	67.8	294.6	66.2
289.3	70.2	289.3	68.8	290.3	67.2	298.0	66.2
289.3	69.6	291.9	68.7	292.3	67.2	298.6	65.4
292.1	69.9	292.6	68.5	294.0	67.0	302.2	64.4
293.1	69.5	296.7	68.0	297.9	66.8	302.4	65.9
294.0	69.5	298.6	67.2	298.5	66.5	302.5	65.7
297.0	69.1	298.8	66.9	301.6	66.3	304.8	64.6
297.0	69.3	302.6	67.1	302.5	66.3	306.4	65.6
298.4	69.1	306.1	66.7	303.3	66.3	306.9	65.2
302.2	68.2	307.5	66.0	303.9	66.1	311.4	64.6
303.0	67.6	311.7	66.4	306.6	65.8		
303.2	67.8			307.2	65.8		
306.8	67.2			307.7	65.8		
307.8	67.5			310.9	65.6		
310.6	66.8			311.1	65.1		
311.6	66.7						

compound (in mN/m). A is the surface area (m^2), R_m is the molar gas constant (used as 8.31451 J/K in the equations[47]), T is the absolute temperature, and P is the pressure. $U_{ij} - U_{ii}$ is related to the difference in the molar interaction energy between the molecule pairs ij and ii in the mixture. The pure liquid adipic acid surface tension was estimated using the method of Macleod–Sudgen,[48] and a linear equation

$$\sigma_2 = A - BT \tag{4}$$

where A and B are parameters was fitted to the estimated points.

2.2.2. Modeled Evaporation and Saturation Vapor Pressures of Adipic and Malonic Acids. We modeled the evaporation of the binary droplets with an evaporation model that takes into account the transitional corrections, as well as the effect of droplet curvature (Kelvin effect) on the evaporation rates.[39−41,49] The UNIFAC Dortmund model[50,51] was used for the activity predictions. The activity model, together with the relative humidity, defines also the calculated droplet composition at the beginning of the flow reactor. The model finds the steady-state composition corresponding to the ambient relative humidity typically during the first iteration step, as the time scale for the water vapor equilibration is of the order of milliseconds at the investigated relative humidities. The transition regime corrections were calculated according to Fuchs and Sutugin,[52] where the mass and thermal accommodation coefficients were assumed to have unity values for all of the studied compounds. For a detailed description of the relationship between mass accommodation and uptake coefficients, see Kulmala and Wagner.[53] The physicochemical properties of the acids used in the model calculations are listed in Table S1, and plots of the water and acid activities according to the UNIFAC Dortmund predictions are presented in Figure S1, both available as Supporting Information. The surface tension and density parametrizations presented by Hyvärinen et al.[27] were used for malonic acid. For adipic acid, we used the surface tension parametrization presented in this work, and the density of adipic acid aqueous solution was approximated with a weighted average of the pure component densities. The saturation vapor pressure values for the pure subcooled malonic and adipic acid were inferred from each data set (corresponding to different temperatures and relative humidities) by matching the modeled evaporation with the experimentally observed reduction in the particle diameter. A temperature-dependent expression of the form

$$\ln P_{\mathrm{sat,l}}/(\mathrm{Pa}) = a - \frac{b}{T} - c \ln T/(\mathrm{K}) \tag{5}$$

was then fitted to the data taking also into account the normal boiling points of the acids. In eq 5, a linear temperature dependence of the vaporization enthalpy ΔH_{vap} (in J/mol)

$$\Delta H_{\mathrm{vap}} = R(b - cT) = \Delta H_{\mathrm{vap}}(T_{\mathrm{b}}) + \Delta c_{\mathrm{p,lv}}(T_{\mathrm{b}})(T - T_{\mathrm{b}}) \tag{6}$$

is assumed, where R is the molar gas constant (8.31451 J/mol/K), T_{b} is the boiling point (K), and $\Delta c_{\mathrm{p,lv}}$ (J/mol/K) is the change in heat capacity upon the gas–liquid-phase transition. The fits were constrained by forcing eq 6 to yield the same vaporization enthalpies at the boiling point $\Delta H_{\mathrm{vap}}(T_{\mathrm{b}})$ as reported in the literature[54,55] and in Table S1 in the Supporting Information. Also, it was assumed that the sign of $\Delta c_{\mathrm{p,lv}}$ is negative to further guarantee the fits to be physically reasonable.

3. Results and Discussion

3.1. Surface Tensions. The measured surface tensions of adipic acid aqueous solution are presented in Table 1 for different adipic acid mole fractions at $T = 298$ K. The surface tension measurements as a function of temperature ($T = 280$–312 K) are presented in Table 2 for four adipic acid mole fractions. The corresponding fitting parameters A, B, $U_{12} - U_{11}$, $U_{21} - U_{22}$, $(\partial(U_{12} - U_{11})/\partial A)_{T,P,X}$, and $(\partial(U_{21} - U_{22})/\partial A)_{T,P,X}$ (see eqs 1–4) are presented in Table 3.

Figure 1a,b shows the measured points along with the corresponding fits as a function of the adipic acid mole fraction at 298 K. In Figure 1a, the results are presented in the whole mole fraction scale, taking into account the data points calculated for the pure acid. Figure 1b shows the measured points and the

TABLE 3: Fitting Parameters for Adipic Acid Surface Tension Data[a]

A (mN/m)	B (mN/m/K)	$U_{12} - U_{11}$ (J)	$U_{21} - U_{22}$ (J)	$(\partial(U_{12} - U_{11})/\partial A)_{T,P,X}$ (J/m^2)	$(\partial(U_{21} - U_{22})/\partial A)_{T,P,X}$ (J/m^2)
58.592	0.083	−16535.39	8392.088	−8.014303	−703.0901

[a] See eqs 1 and 4.

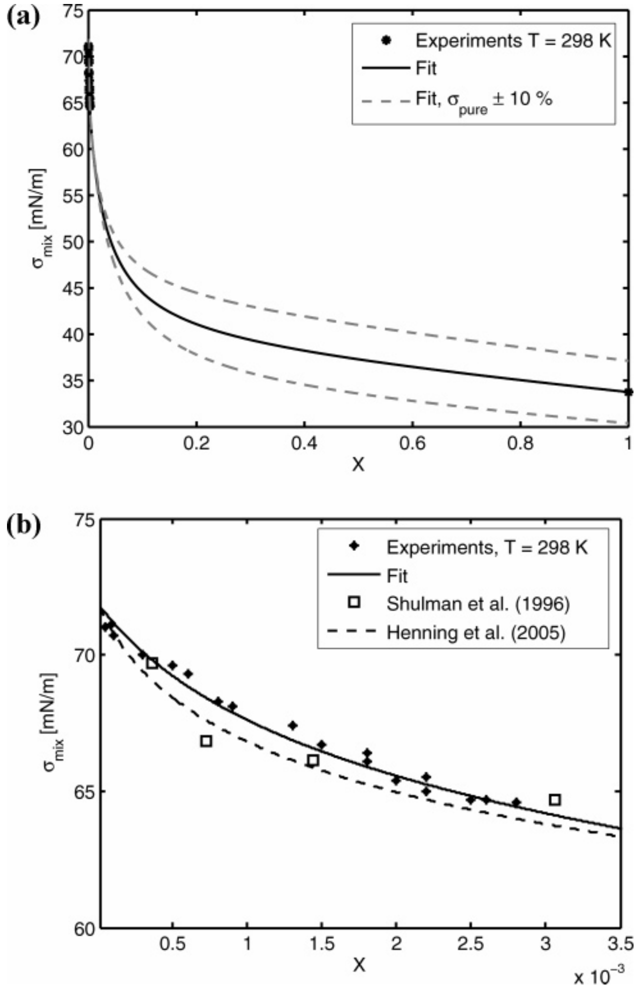

Figure 1. Surface tension of adipic acid aqueous solution as a function of adipic acid mole fraction. Asterisks refer to measurement data (except for the pure acid value, which has been calculated[48]) and solid lines to the fitted curve. Squares indicate the data points reported by Shulman et al.,[16] and a corresponding fit to this data by Henning et al.[19] has been indicated with a dashed line. Fitted curves corresponding to maximum uncertainty of 10% in pure acid surface tension are included in panel a (dashed gray lines). In the measurement range considered here (indicated in panel b), however, the fits coincide.

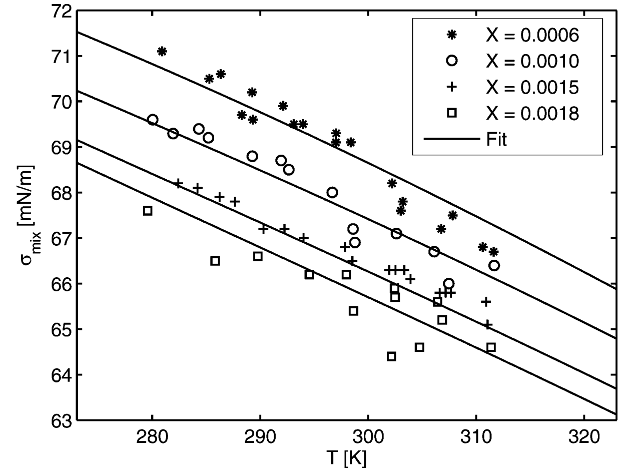

Figure 2. Surface tension of adipic acid aqueous solution as a function of temperature for four different compositions (asterisks: $X = 0.0006$; circles: $X = 0.0010$; crosses: $X = 0.0015$; and squares: $X = 0.0018$) and the corresponding fitted curves.

TABLE 4: Average Temperatures (*T*), Relative Humidities (RH), Total Droplet Concentrations (*C*), and Their Standard Deviations in Laminar Flow Reactor and Saturation Vapor Pressure Values (P_{sat}) for Each Data Set for Malonic (a) and Adipic (b) Acid

(a) Malonic acid

data set	*T* (K)	RH (%)	*C* (cm^{-3})	$p_{sat,l}$ (10^{-4} Pa)
1[a]	299.08 ± 0.03	68.6 ± 0.4	8803 ± 434	9.5 ± 1.4
2[a]	299.39 ± 0.03	58.2 ± 0.9	156 ± 8	8.5 ± 1.3
3	293.26 ± 0.10	58.9 ± 0.4	318 ± 16	1.2 ± 0.2
4	293.51 ± 0.37	67.1 ± 2.8	302 ± 206	2.5 ± 0.4
5	293.49 ± 0.10	68.4 ± 2.0	1295 ± 204	1.9 ± 0.3
6	293.04 ± 0.89	75.3 ± 6.2	929 ± 172	2.0 ± 0.3
7	294.88 ± 0.09	58.1 ± 0.6	182 ± 51	2.6 ± 0.4
8	294.16 ± 0.19	65.1 ± 1.2	153 ± 137	2.4 ± 0.4

(b) Adipic acid

data set	*T* (K)	RH (%)	*C* (cm^{-3})	$p_{sat,l}$ (10^{-4} Pa)
1	297.95 ± 0.15	78.5 ± 0.6	5000 ± 2160	2.8 ± 0.4
2	298.96 ± 0.02	79.9 ± 0.5	21 ± 4	1.7 ± 0.3
3	294.45 ± 0.06	68.5 ± 0.4	4767 ± 880	1.3 ± 0.2
4	293.75 ± 0.30	79.8 ± 1.4	587 ± 231	0.9 ± 0.1
5	297.71 ± 1.01	64.8 ± 0.5	592 ± 47	1.9 ± 0.3
6	295.37 ± 0.24	59.0 ± 0.9	366 ± 52	0.6 ± 0.1
7	295.64 ± 0.28	58.7 ± 1.4	108 ± 8	0.9 ± 0.1
8	295.41 ± 0.33	66.4 ± 3.1	84 ± 9	1.2 ± 0.2
9	295.47 ± 0.15	77.1 ± 1.9	87 ± 9	1.0 ± 0.2

[a] First two measurement points have been presented also by Koponen et al.[40]

fitted curve on a smaller scale, as well as a comparison to the available literature data on the surface tension of the adipic acid aqueous solution. The surface tension expression obtained in this study is compared to the four data points reported by Shulman et al.[16] and the corresponding fitted expression[19] at 298 K. It can be seen that the expression obtained in this study agrees relatively well with the previous data, the values obtained in this study being slightly (approximately 1%) higher than the previously reported ones.

The temperature-dependent data and fitted curves are presented in Figure 2. It can be seen that the addition of adipic acid reduces the surface tension of water quite significantly, even at mole fractions clearly below the solubility limit (~0.003). For instance, at a mole fraction of 0.002, the surface tension is reduced to 65.4 mN/m, which is a reduction of 9% as compared to the value of pure water.

3.2. Saturation Vapor Pressures. The average temperatures, relative humidities, and droplet concentrations along with their standard deviations in the laminar flow reactor during each data set on the evaporation rates of the solution droplets are presented in Table 4a (malonic) and Table 4b (adipic). The saturation vapor pressures obtained from the model fits for each evaporation rate experiment are also presented. As expected, the obtained saturation vapor pressure values show temperature dependence, typically increasing with increasing temperature. It can also be noted that the saturation vapor pressure values for malonic acid are consistently higher than for adipic acid. However, for both acids, the vapor pressures are of the order of 10^{-4} Pa at the studied temperatures. No clear dependence on the droplet concentration is observed.

Uncertainties related to the vapor pressure values result from uncertainties in both the experiments and the modeled evaporation. From the experimental point of view, for example, inhomogenities in the temperature, RH, droplet concentration, and flow profiles in the laminar flow tube may introduce some error to the results. In the model calculations, the main sources of uncertainty are possible inaccuracies in the thermodynamic properties such as the activities and diffusion coefficients of the acids. Also, in the model calculations, a monodisperse

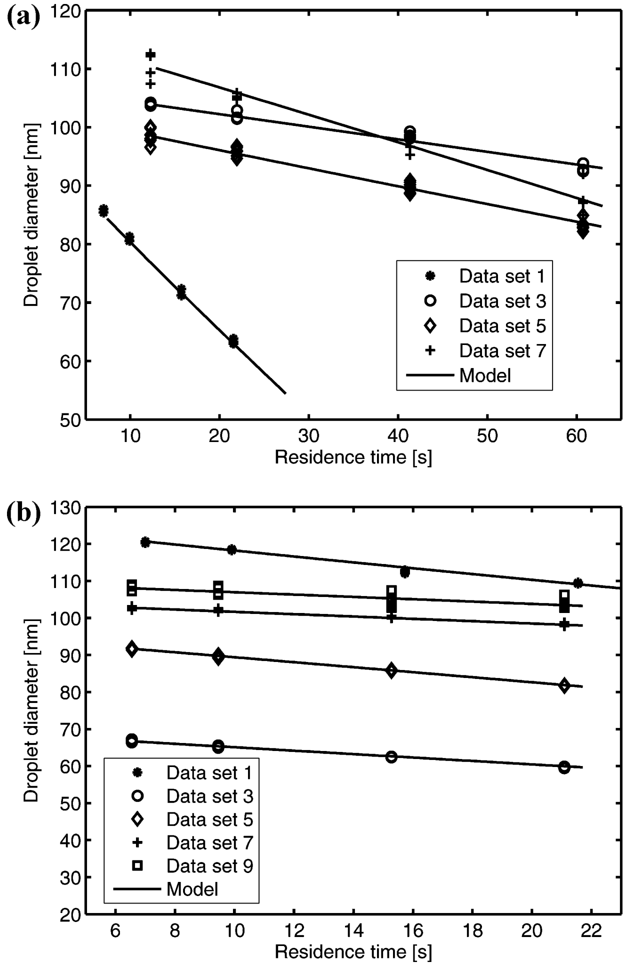

Figure 3. Measured (markers) and modeled (lines) diameters of malonic (a) and adipic (b) acid aqueous solution droplets as a function of their residence time in the laminar flow reactor. Details of the data sets are presented in Table 4. Modeled curves correspond to the saturation vapor pressure values listed in Table 4.

droplet mode is assumed. It is very difficult to provide any reliable uncertainty estimates for, for example, the accommodation and activity coefficients used in the calculations, as no general reference data exist. Yet, these variables affect the derived results significantly. The experimental uncertainties typical to the used system have been broadly discussed by Koponen et al.[40] and are approximately ±15%, whereas the sensitivity of the model calculations to different physical parameters has been demonstrated by Riipinen et al.[39]

Selected examples of the measured and corresponding modeled evaporation rates of the solution droplets are presented in Figure 3a (malonic) and Figure 3b (adipic). The modeled curves in Figure 3 correspond to the best match cases, where the values listed in Table 4 have been used for the subcooled liquid vapor pressures of the acids. For each of the evaporation rate experiments, the reduction of the droplet size was rather linear in time over the time span studied, and the modeled results caught the features of the evaporation process well. It can also be seen from Figure 3 that the droplet diameters corresponding to each sampling port stayed relatively constant (average standard deviation of the droplet diameter being 0.8 nm) throughout each evaporation rate measurement, indicating also stable conditions in the flow tube.

The vapor pressure values obtained from the evaporation rate data are presented as a function of temperature in Figure 4a (temperature range close to the measurement temperatures) and Figure 4b (temperature range including the normal boiling points of the acids). The subcooled liquid vapor pressure of malonic acid reported by Zardini et al.[42] is also shown but not included in the fit. The temperature-dependent expressions fitted according to eq 5 for the saturation vapor pressures are presented as solid lines in Figure 4b. The corresponding mass concentrations (in μg/m^3) calculated using the ideal gas law and the molar masses of the acids are shown by dashed lines in Figure 4b. Again, it can be noted that the vapor pressure of malonic acid is somewhat higher as compared to that of adipic acid, consistently with the lower boiling point of malonic acid. The fitting parameters a, b, and c for the subcooled saturation vapor pressure and latent heat of evaporation expressions (eqs 5 and 6), along with the corresponding values for latent heat of evaporation at 298 K and $\Delta c_{p,lv}$, are reported in Table 5.

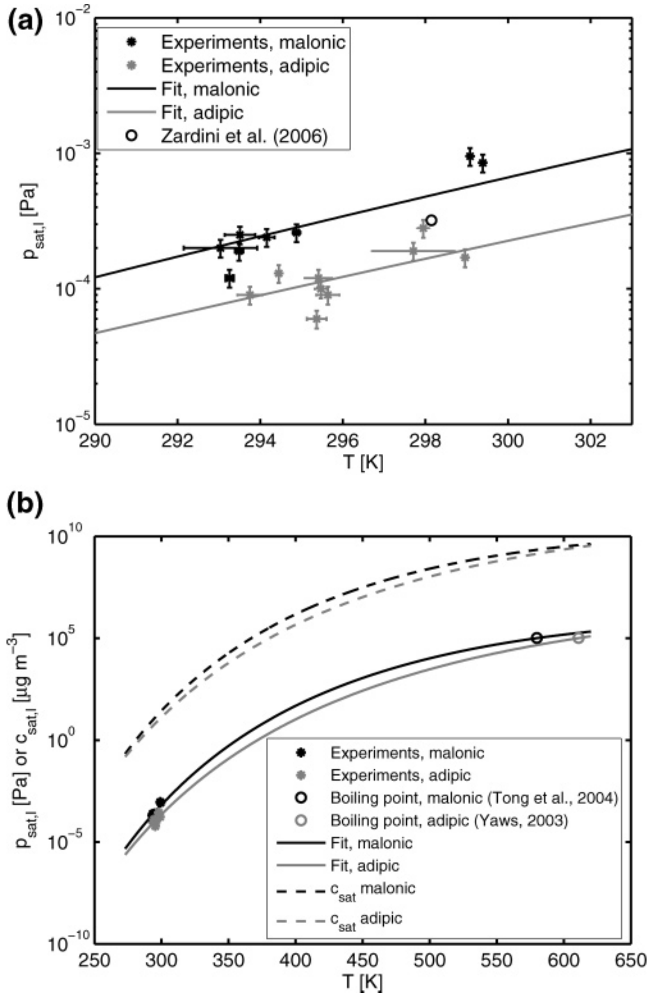

Figure 4. Subcooled liquid-phase saturation vapor pressures of malonic (black) and adipic (gray) acids. Asterisks refer to the experimental points (see Table 4), the open circle in panel a marks the data point by Zardini et al.,[42] and in panel b, the normal boiling point and lines correspond to the fitted expressions. In panel a, the results are presented in a temperature scale close to the measurement temperatures. Panel b presents results in a temperature scale including the normal boiling point, and the saturation mass concentrations (μg/m^3) are indicated with dashed lines. Data reported by Koponen et al.[40] are also included in the figure.

In Figure 5, the subcooled liquid vapor pressures of C3−C6 dicarboxylic acids reported in this study (malonic and adipic) and our previous study[40] (succinic and glutaric) are presented along with a representative selection of the available literature data at 298 K[30−35] (see also Table 5). The error bars presented in Figure 5 for the vapor pressure expressions determined in

TABLE 5: Parameters for Temperature-Dependent Expressions of C3−C6 Dicarboxylic Acid Saturation Vapor Pressures and Derived Thermodynamic Properties at 298 K[a]

acid	a	b (K)	c	ΔH_{vap} (298 K) (kJ mol^{-1})	$\Delta c_{\text{p,vl}}$ (T_b) (J mol^{-1} K^{-1})	$p_{\text{sat,l}}$ (298 K) (10^{-4} Pa)	$p_{\text{sat,s}}$ (298 K) (10^{-5} Pa)
malonic	220.2389	22634.96	26.668	122.1 ± 24.8	−221.7	4.9 ± 1.0	5.2 ± 1.1
succinic[b]	119.3281	16278.44	12.576	104.3 ± 23.1	−104.6	9.9 ± 2.4	2.5 ± 0.6
glutaric[b]	125.7550	16776.98	13.489	106.1 ± 23.2	−112.0	7.1 ± 2.2	18.7 ± 5.9
adipic	140.6704	18230.97	15.480	113.2 ± 21.8	−128.7	1.7 ± 0.3	0.4 ± 0.1

[a] Uncertainty estimated for ΔH_{vap} (298 K) and $\Delta c_{\text{p,vl}}$ (T_b) have been obtained from fits assuming 10% uncertainty for boiling points of acids[55] and worst case uncertainties of saturation vapor pressure and temperature data derived from our measurements. $\Delta c_{\text{p,vl}}$ (T_b) are estimated to be correct within a factor of 2. Error estimates for vapor pressure values represent the average deviations between vapor pressures obtained from evaporation rate measurements and fitted temperature-dependent expressions. [b] From Koponen et al.[40]

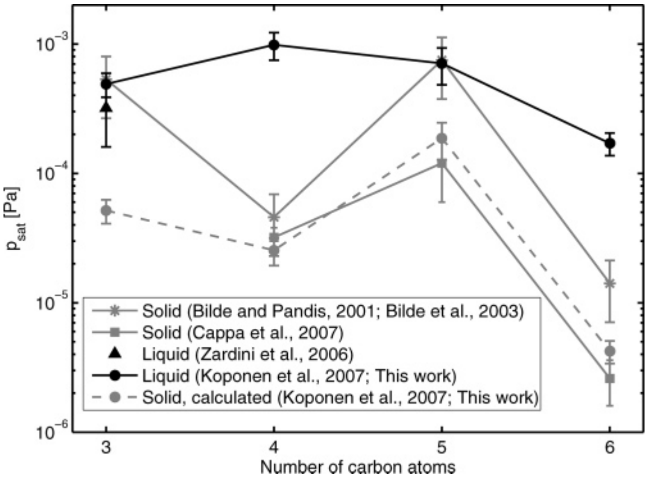

Figure 5. Saturation vapor pressures of carbon number 3−6 dicarboxylic acids at $T = 298$ K. Black markers: subcooled liquid state (Zardini et al.,[42] Koponen et al.,[40] and this work). Gray markers: solid state (Bilde and Pandis,[31] Bilde et al.,[32] and Cappa et al.;[35] values estimated from the liquid-phase data obtained in this work). Error bars for the values presented in this work and in Koponen et al.[40] represent average deviations between vapor pressures obtained from evaporation rate measurements and fitted temperature-dependent expressions.

this work and in Koponen et al.[40] represent the average deviations between the vapor pressures obtained from the evaporation rate data sets and the fitted temperature-dependent expressions.

First, the subcooled liquid saturation vapor pressure of malonic acid of (4.9 ± 1.0) × 10^{-4} Pa at 298 K reported in this study is compared to the corresponding subcooled liquid value of (3.2 ± 1.2) × 10^{-4} Pa presented by Zardini et al..[42] It is observed that the values are of similar magnitude, taking into account the uncertainties related to both studies. To the best of our knowledge, no subcooled liquid-state vapor pressures of other dicarboxylic acids other than those reported by Riipinen et al.[39] and Koponen et al.[40] exist.

Second, a comparison is made with the experimentally derived solid-state vapor pressures at 298 K. As mentioned in the Introduction, solid-state vapor pressures of C4−C10 dicarboxylic acids have been reported in the literature using several different experimental techniques.[30−35] For clarity, we show only the vapor pressures reported by Cappa et al.,[35] Bilde et al.,[32] and Bilde and Pandis,[31] as they represent well the range of the reported solid-state vapor pressures, as well as two different experimental methods where the latter is essentially the same as used in this study. It can be seen from Figure 5 that the subcooled liquid-state saturation vapor pressure values are higher than or similar to the solid-state values and that they do not follow the even−odd carbon number alternation pattern as has been observed for the solid state.[30−35] This is reasonable as the alternation has been related to properties of the crystal structure of the acids,[32,33,55,56] which are not naturally present in the liquid phase. The subcooled liquid-phase vapor pressures determined in this work are consistently higher than the values reported by Cappa et al.[35] and the solid-state values of the even acids reported by Bilde et al.[32] For the odd acids (malonic and glutaric), the liquid-phase values are very close to the solid-state values reported by Bilde and Pandis[31] and Bilde et al.[32] The clear difference between the solid-phase values and the values reported here also gives us confidence that we have studied aqueous solution droplets, also in the case of adipic acid.

In Figure 5 and Table 5 we also present the solid-state values calculated from the liquid-phase data determined in this study and in Koponen et al.[40] using the formula[57]

$$\ln \frac{P_{\text{sat,l}}}{P_{\text{sat,s}}} = \frac{\Delta H_{\text{fus}}}{RT_{\text{m}}}\left(\frac{T_{\text{m}}}{T} - 1\right) - \frac{\Delta c_{\text{p,sl}}}{R}\left(\frac{T_{\text{m}}}{T} - 1\right) + \frac{\Delta c_{\text{p,sl}}}{R} \ln \frac{T_{\text{m}}}{T} \quad (7)$$

where s refers to the solid and l to the liquid phase, T_{m} is the normal melting point, ΔH_{fus}[48,54] is the enthalpy of fusion in the melting point, and $\Delta c_{\text{p,sl}}$[48,54,58] refers to the change in heat capacity upon melting. The thermodynamic properties used in the calculations are listed in the Supporting Information in Table S1. The solid-state values calculated from the liquid-phase data reported in this work and the work by Koponen et al.[40] seem to agree well with the solid-state values reported by Cappa et al.[35] and also with the solid-state value reported by Zardini et al.[42] of (4.1 ± 1.6) × 10^{-5} Pa but tend to be consistently smaller than the values of Bilde and Pandis[31] and Bilde et al.,[32] except for succinic acid.

Zardini et al.[42] suggested that the solid-state vapor pressure of malonic acid measured by Bilde et al.[32] may in fact be the subcooled liquid vapor pressure. This cannot be excluded since Peng et al.[36] have observed neither deliquescence nor crystallization in electrodynamic balance studies of malonic acid. For succinic and glutaric acids, the TDMA experiments of Bilde et al.[32] were, however, performed well below the crystallization relative humidities[36] of the acids. Also, the succinic and adipic acid particles dried in diffusion dryers and by dilution with dry air under ambient conditions have been shown to behave as solids in cloud droplet formation experiments.[20] Another explanation is therefore needed.

Cappa et al.[35] dried their particles by passing them through a flow tube with a molecular sieve followed by preheating the collected aerosol particles, whereas the particles studied by Bilde et al.[32] and Bilde and Pandis[31] were dried under ambient conditions in diffusion dryers and by dilution with dry air. Cappa et al.[35] speculated on the differences between their work and the work by Bilde and Pandis,[31] Bilde et al.,[32] and Chattopadhyay and Ziemann.[34] They suggested that preheating the sample is essential for complete drying and sintering of the particles, as the obtained vapor pressure values can be significantly affected by water molecules trapped in the diacid sample—even in spite of careful drying of the aerosol. This suggestion deserves further investigation, as does the possible amount and role of other nonvolatile impurities that can be present in the particles and potentially affect the determined vapor pressure values.

Atmospheric particles may be solid, liquid, amorphous, or a combination of the three, and it is not clear which phase is predominant or in which phase the dicarboxylic acids exist in the real atmosphere. To elucidate this issue, knowledge on the magnitudes of both solid and subcooled liquid-phase vapor pressures is useful. It is clear from Figure 5 that the difference between the subcooled liquid and the solid-state vapor pressures may span several orders of magnitude. It can also be seen that the solid-state values derived from different measurement techniques are not quite consistent. Solid-state saturation vapor pressures cannot exceed those over the pure liquid phase. Therefore, based on the previous discussion, we believe that the likely range of solid-state vapor pressures of the C3−C6 diacrboxylic acids is given in Figure 5. On the basis of this work and the work by Zardini et al.,[42] the subcooled liquid-state vapor pressures of the C3−C6 dicarboxylic acids are in the range of 10^{-4} to 10^{-3} Pa (20−50 μg m^{-3}).

The ΔH_{vap} (298 K) values for succinic, glutaric, and adipic acids are 10, 3, and 8% higher than the corresponding values reported by Roux et al.,[29] respectively. The ΔH_{vap} (298 K) values from this study and from the study by Koponen et al.[40] are lower than most of the correspoding sublimation enthalpies reported in the literature.[30−35] However, in the case of the odd (malonic and glutaric) acids, the values reported in Table 5 exceed the sublimation enthalpies reported by Bilde et al.[32] and Tao and McMurry.[30] This is the case also comparing our values with the sublimation enthalpies of malonic acid reported by Ribeiro da Silva et al.[33] This observation also supports the speculation that, in particular in the case of odd acids, the experimental method of drying can affect the evaporation rates and the obtained vapor pressure and vaporization enthalpy values. The $\Delta c_{p,\mathrm{lv}}$ values reported in Table 5 are somewhat higher as compared to the literature data. For malonic acid, the deviation from the value by Tong et al.[55] is 136%, whereas for succinic, glutaric, and adipic acids, the deviations are much smaller, being 5% (succinic), 6% (glutaric), and 30% (adipic). The deviations from values reported by Roux et al.[29] are 44% (succinic), 38% (glutaric), and 44% (adipic). The relatively high values for the malonic acid vaporization enthalpies might result from, for example, uncertainties in the experiments and modeling but also in the boiling point reported in the literature.

4. Conclusion

We measured the surface tension of adipic acid aqueous solutions at atmospherically relevant temperatures and several adipic acid mole fractions. The data presented in this work are to our knowledge the most extensive data set on the subject. A parametrization based on the data has also been reported, and the agreement between the measured data points and the fitted expression is satisfying, looking at the surface tension of the water−acid mixture as a function of both adipic acid mole fraction as well as temperature. The results show that adipic acid significantly reduces the water surface tension even at mole fractions smaller than the solubility limit (∼0.003). The reported results agree well with the available literature,[16,19] the surface tension values reported here being slightly higher (on average 1%) than those found in the previous works. It should be noted, however, that our results are based on more than 80 independent measurements, whereas the previous experimental data presented by Shulman et al.[16] contain only four data points in total. The comprehensive description of the surface tension of adipic acid aqueous solutions gives more confidence on predictions of the cloud droplet activity of adipic acid containing aerosols.

Evaporation rates of aqueous solution droplets containing malonic or adipic acids were also measured at temperatures close to atmospheric conditions. We analyzed the evaporation data with a binary evaporation model to determine the temperature-dependent saturation vapor pressures of subcooled liquid-phase malonic and adipic acids. Temperature-dependent expressions were fitted to the saturation vapor pressure data, and the parameters for the expression have been reported. The obtained values for the vapor pressures of liquid malonic and adipic acid are of the order of 10^{-4} Pa at atmospheric temperatures. The saturation vapor pressure of subcooled liquid-phase malonic acid agrees reasonably well with the corresponding value reported by Zardini et al.,[42] which, apart from our own studies, is so far the only measurement on the subcooled liquid vapor pressures of dicarboxylic acids at atmospheric temperatures that we know of in current literature.

We compared the subcooled liquid saturation vapor pressures reported in this study and in our previous work[40] with the values reported in the literature for the solid-state vapor pressures of C3−C6 dicarboxylic acids.[30−35] According to our observations, the liquid-state saturation vapor pressures do not seem to alternate with the parity of the carbon number of the acid, as has been observed for solid-state values. This is reasonable as the alternation has been related to the properties of the crystal structure of the acids,[32,33,55,56] which naturally is not present in the liquid phase. If the liquid-phase values reported in this work are used to calculate estimates for the solid-phase vapor pressures, a fairly good agreement with the solid-state values reported by Cappa et al.[35] and Zardini et al.[42] is found, whereas the values for the odd dicarboxylic acids in particular are lower than the values reported by Bilde and Pandis[31] and Bilde et al..[32] The difference in the solid-state vapor pressures seems to be related to the way the particles were generated in the laboratory. In the real atmosphere, however, the particles are likely to be neither pure nor heated to high temperatures. If the evaporation rate depends on the way the particles are generated and dried, this may have important consequences in interpreting the laboratory experiments as well as atmospheric data. The large difference between the solid-state and the liquid-state vapor pressures (see Figure 5) highlights the importance of elucidating the actual phase of atmospheric particles.

The surface tension and saturation vapor pressure determinations presented in this work complete the series of C3−C6 staight-chain dicarboxylic acid aqueous solution surface tension and subcooled liquid-phase vapor pressure data sets, started by the works of Hyvärinen et al.[27] with surface tensions of C3−C5 dicarboxylic acids and Riipinen et al.[39] and Koponen et al.[40] with temperature-dependent vapor pressure expressions of subcooled liquid C4−C5 diacids and preliminary data on malonic acid. The liquid-phase vapor pressures and the solution surface tensions are key properties in describing the formation and growth as well as cloud droplet activation properties of aerosols containing dicarboxylic acids.

In this work, we concentrated on the binary solutions of water and selected dicarboxylic acids. The atmospheric particulate phase, however, is likely to contain multiple additional compounds and phases. Therefore, in the future, a logical step forward is to investigate the properties of multicomponent solutions containing dicarboxylic acids and other relevant organic compounds. Also, data on multifunctional organic compounds are needed for more accurate information on the properties of atmospheric organics.

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Supporting Information Available: Table S1: physicochemical properties of malonic and adipic acids used in the calculations. Figure S1: water and acid activities according to the UNIFAC Dortmund activity model. This information is available free of charge via the Internet at http://pubs.acs.org.

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