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Surface Tensions and Densities of Oxalic, Malonic, Succinic, Maleic, Malic, and *cis*-Pinonic Acids

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The surface tensions and densities of aqueous solutions of oxalic, malonic, succinic, maleic, malic, and *cis*-pinonic acids were measured as a function of the acid mole fraction at 25 °C. These organic acids are typically found in atmospheric aerosols. The surface tensions were measured using the Wilhelmy plate method and were measured also as a function of temperature. The measurable mole fractions were limited by the solubilities of the acids at room temperature. All the acids lower the surface tension of pure water. *cis*-Pinonic acid lowers the surface tension most effectively. The measured surface tensions were fitted with equations covering the acid mole fraction range from zero to one and assuming a theoretical surface tension of pure, supercooled acids at room temperature. The measured densities were also fitted in a similar way. These equations can be used in model calculations of formation and growth of atmospheric particles.

Introduction

A significant fraction of atmospheric particulate matter consists of organic material,[1] either of primary or secondary origin. Different processes in the aerosol life cycle involving organics have not yet been thoroughly investigated. Organic compounds are likely to have a central role in the formation and initial growth of atmospheric aerosol particles.[2] It has been suggested that organic vapors contribute to the condensational growth of freshly nucleated particles,[3] which are often assumed to contain sulfuric acid.[4] Organic aerosol particles can also act as cloud condensation nuclei (CCN) and play a part during the cloud droplet activation.[5,6] Some of the identified organic species are di- and polycarboxylic acids, which can effectively reduce the surface tension of CCN.[7]

Thermodynamic properties of organic compounds in the atmosphere are poorly known due to the vast diversity of compounds involved. The lack of reliable thermodynamic data, such as surface tension and vapor pressure, is an obstacle for detailed theoretical and experimental studies of different aerosol processes. This is stressed for example by Gaman et al., who have calculated homogeneous nucleation rates for water + succinic acid and water + glutaric acid mixtures.[8] The properties of a small aerosol particle can be very different from those of the corresponding bulk liquid. The surface tension is an important parameter in the Kelvin equation,[9] which describes how the curvature effect changes the partial vapor pressure of a small droplet from the bulk value.

Organic acids are among the common type of organic compounds in the atmosphere. Secondary photochemical formation is speculated to be an important source of particles containing low molecular weight dicarboxylic acids such as oxalic, malonic, and succinic acids.[10] Malonic, maleic, and malic acids have also been found in particulate matter, for example, from biomass burning.[11] *cis*-Pinonic acid is an oxidation product of α-pinene emitted from trees and is found both in the gas and aerosol phase.[12] Some experimental data of the thermodynamic properties of organic acids are available. For example, Shulman et al.[6] have measured the solubilities and surface tensions of malonic, glutaric, succinic, oxalic, adipic, phthalic, and *cis*-pinonic acids. Lately, Tuckermann and Cammenga[13] have measured the surface tensions of aqueous solutions of levoglucosan, 3-hydroxybutanoic acid, 3-hydroxybenzoic acid, azelaic acid, pinonic acid, and humic acid. However, more measurements of different compounds are needed. Here we present the surface tensions and densities of the aqueous solutions of oxalic, malonic, succinic, maleic, malic, and *cis*-pinonic acids.

Experimental Methods

The surface tensions were measured with a thermostated tensiometer (Digital Tensiometer K 10ST, Krüss Gmbh, Germany) using a Wilhelmy plate method.[14] The temperature was set to 25 °C and controlled with a circulation liquid path (Lauda RC6 CS). The molecular weights, solubilities, purities, and manufacturers of the acids used are presented in Table 1. All acids were dissolved in water. Water was purified to ultrapure quality (Milli-Q, 18 M).

The aqueous samples were prepared by mass in Pyrex bottles and mixed until all the acid was dissolved. Prior to weighting and dilution, all the acids were dried in an oven at a temperature below their melting points to evaporate any volatile impurities, such as water vapor and ammonia. Substances were weighted with a Precisa junior 310M balance (absolute accuracy 0.002 g) with an uncertainty of about 0.1 %. This corresponds to an uncertainty of 0.1 % in mole fraction. In a typical surface tension measurement, a sample with a volume of about 20 mL was inserted in the tensiometer in a glass container. The platinum plate was submerged in the sample and the measurement performed immediately. Measurements were performed up to each compound's solubility limit (see Table 1). The tensiometer

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Table 1. Some Properties of the Measured Organic Acids

acid	oxalic[a]	malonic	succinic	maleic	malic	*cis*-pinonic
molecular formula	$C_2H_2O_4$	$C_3H_4O_4$	$C_4H_6O_4$	$C_4H_4O_4$	$C_4H_6O_5$	$C_{10}H_{16}O_3$
molecular weight, g/mol	90.03	104.06	118.09	116.07	134.09	184.23
solubility (g of solute/100 g of water)	12[b]	161[b]	8.8[b]	80.4[b]	145[b]	0.37[c]
purity, %	>99.5	>99	ACS quality	>99	>99	>98
manufacturer	J. T. Baker	Fluka	J. T. Baker	Fluka	Acros	Aldrich

[a] Oxalic acid was provided as a dihydrate form. [b] Ref 1 at 25 °C. [c] Ref 6 at 0 °C.

Table 2. Parameters for Equations 1, 3, and 4

acid	A	B	C	D	E	F	G	H
oxalic	87.91	0.12	−0.095580	0.13935	0.7408	7.1712	0.9999	1.0003
malonic	87.00	0.13	−0.301717	0.073139	4.1950	13.658	0.9984	0.9929
succinic	83.45	0.12	−0.101554	0.024195	4.4768	41.333	1.0000	1.0082
maleic	83.31	0.12	−0.121102	0.033532	3.8087	29.878	0.9969	0.9867
malic	83.00	0.11	−0.052418	0.005632	9.5337	177.69	0.9999	0.9974
cis-pinonic	49.74	0.06	0.006682	0.014794	47.127	5896.64		

was first tested by comparing measured surface tensions of 1-alcohols to their literature values at 25 °C. All the measured values were found to be within 0.5 % of the literature values.[15] The same comparison was made against water. The measured surface tensions of distilled water were from 71.6 to 72.3 mN/m compared to the literature value of 72.0 mN/m at 25 °C.[16] The total uncertainty of the surface tension measurements was estimated to be less than 1.0 %.

Temperature-dependent surface tensions were also measured. For this, the samples were set to the desired temperature in the circulation liquid reservoir in the closed Pyrex bottles. The sample was then inserted in the tensiometer, which was thermostated by the same circulation liquid. Air conditioner was applied to ensure that the room temperature is as close as possible to the measurement temperature. The temperature of the liquid surface was measured before and after the measurement with a Hg-thermometer (Amarell). The measurement setup used does not offer a completely closed, isothermal system, and the temperature of the sample is therefore affected by the room temperature. Also, there is a temperature gradient between the platinum plate and the liquid surface. The temperature-dependent measurements are limited by the difference of the room and the sample temperatures, precipitation of the sample at low temperatures, and evaporation of the sample at high temperatures. The temperature range of the measurements was 10 to 30 °C. The uncertainty of the thermometer was 0.2 °C. The total uncertainty in temperature was estimated to be ± 0.5 °C at most, depending on the temperature of the sample.

The density measurements were performed at 25 °C directly after the surface tension measurements were made. A small sample volume of 10 to 15 mL was collected from the solution used in the surface tension measurement with a volumetric pipet and weighted. The accuracy of the density measurements was tested with purified water at 25 °C. The measured densities were within 0.5 % of the literature values.[16] The uncertainty of the volumetric pipets was 0.03 mL. The same weighting balance was used as before (Precisa Junior 310M). Total uncertainty of the density measurements was estimated to be less than 0.5 %.

Results and Discussion

Surface Tensions. The surface tension data for atmospheric model calculations is often needed outside the solubility limits of the experiments. To overcome this problem, the measured surface tensions were fitted to equations, which could be extrapolated beyond the solubility limits. The surface tensions of the pure acids were obtained by using the method of Macleod−Sugden presented in Reid et al.[17] The Macleod−Sugden method estimates the surface tensions of hydrogen-bonded liquids with errors normally less than 5 to 10 %. At room temperature the acids are solids, and it is logical to assume supercooled substances. This will certainly increase the error in the estimation of the surface tension. However, according to a sensitivity analysis by Gaman et al.,[8] the accuracy of the Macleod−Sugden method is still very reasonable for atmospheric nucleation calculations. The supercooled surface tensions were fitted to a linear equation:

$$\sigma_1(T)/\mathrm{mN{\cdot}m^{-1}} = A - B{\cdot}T/\mathrm{K} \tag{1}$$

where σ_1 is the surface tension of pure acid, T is the absolute temperature, and A and B are parameters presented in Table 2 for each acid. The surface tensions of aqueous solutions as a function of the acid mole fractions are obtained by fitting an equation presented by Chunxi et al.[18] to the measured data. The equation presented by Chunxi et al. is

$$\sigma = \sum_i x_i \sigma_i - RT \sum_i \frac{x_i}{\sum_j x_j \Lambda_{ij}} \sum_j x_j \left(\frac{\partial \Lambda_{ij}}{\partial A} \right)_{T,P,x} \tag{2}$$

where x_i is the mole fraction of compound i, R is the universal gas constant, A is surface area, and Λ is a dimensionless parameter related to the molar volumes of the components and to the difference in interaction energy between molecule pairs ij and ii. By using Λ_{ij} and $(\partial\Lambda_{ij}/\partial A)$ as fitting parameters, eq 2 reduces for a binary case to

$$\sigma/\mathrm{mN{\cdot}m^{-1}} = (\sigma_2(T)/\mathrm{mN{\cdot}m^{-1}})(1 - x_1) + (\sigma_1(T)/\mathrm{mN{\cdot}m^{-1}})x_1 - RTx_1(1 - x_1)\left[\frac{C}{x_1 + D(1 - x_1)} + \frac{E}{Fx_1 + (1 - x_1)}\right] \tag{3}$$

where $\sigma_2(T)$ is the surface tension of pure water as a function of temperature,[16] x_1 is the mole fraction of the acid, and C, D, E, and F are fitting parameters presented in Table 2.

The measured surface tensions at 25 °C are presented in Table 3 and in Figures 1 to 3 as a function of x_i. All the measured organic acids lower the surface tension of pure water as a function of increasing acid mole fraction. This corresponds to findings by Facchini et al.,[19] who reported a decrease of surface tension in atmospheric cloudwater samples as a function of the total carbon content in the sample. It can be seen that the ability of the acids to lower the surface tension increases with increasing carbon chain length. Oxalic acid has the least effect, while *cis*-pinonic acid lowers the surface tension most. The same

Table 3. Surface Tensions (σ) and Densities (ρ) of Organic Acids (i = 1) + Water (i = 2) as a Function of Mole Fractions (x_i)

	σ		ρ		σ		ρ
x_1	mN·m^{-1}	x_1	kg·m^{-3}	x_1	mN·m^{-1}	x_1	kg·m^{-3}
Oxalic Acid							
0.0017	71.6	0.002	0.996	0.0098	70.7	0.010	1.019
0.0034	71.4	0.003	1.001	0.0115	70.5	0.012	1.026
0.0050	71.2	0.005	1.008	0.0121	70.7	0.013	1.030
0.0067	71.0	0.007	1.012	0.0131	70.3	0.015	1.034
0.0083	70.7	0.008	1.016	0.0146	70.1		
Succinic Acid							
0.0011	70.9	0.0011	0.991	0.0078	67.6	0.0047	1.002
0.0022	70.0	0.0012	0.997	0.0089	67.3	0.0056	1.001
0.0028	69.8	0.0022	0.993	0.0100	66.6	0.0067	1.002
0.0033	69.4	0.0022	1.003	0.0107	66.9	0.0068	1.008
0.0045	68.9	0.0028	0.996	0.0111	66.4	0.0078	1.005
0.0056	68.5	0.0033	0.997	0.0117	66.7	0.0089	1.007
0.0067	68.1	0.0037	1.001			0.0100	1.009
0.0071	67.7	0.0045	0.998			0.0110	1.010
Malic Acid							
0.003	70.3	0.003	1.006	0.054	68.4	0.096	1.182
0.007	70.1	0.015	1.037	0.058	68.1		
0.015	69.8	0.023	1.051	0.070	67.8		
0.023	69.3	0.032	1.079	0.082	67.3		
0.032	69.3	0.054	1.115	0.087	66.8		
0.043	68.4	0.075	1.146				
Malonic Acid							
0.010	69.2	0.009	1.016	0.080	63.5		
0.017	68.5	0.030	1.054	0.088	64.2		
0.025	66.7	0.041	1.068	0.094	63.5		
0.033	66.7	0.055	1.090	0.107	62.7		
0.040	65.6	0.069	1.108	0.122	62.3		
0.050	65.6	0.085	1.129	0.137	62.2		
0.055	65.5	0.102	1.152	0.149	62.6		
0.065	65.0	0.147	1.196	0.158	62.2		
0.070	64.2						
Maleic Acid							
0.0080	68.0	0.008	1.016	0.0579	61.2	0.094	1.135
0.0116	67.6	0.017	1.031	0.0600	62.3		
0.0170	65.9	0.027	1.048	0.0627	60.4		
0.0267	64.1	0.037	1.063	0.0764	58.8		
0.0374	61.4	0.049	1.084	0.0850	60.3		
0.0376	61.4	0.062	1.103	0.0932	59.7		
0.0489	62.2	0.077	1.121	0.1083	59.5		
Cis-Pinonic Acid							
0.00002	69.5	0.00018	0.995	0.00041	57.2	0.00066	0.994
0.00004	66.8	0.00025	0.993	0.00050	56.3	0.00083	0.997
0.00011	64.4	0.00033	0.995	0.00058	55.8		
0.00018	61.4	0.00041	0.997	0.00065	56.2		
0.00024	61.2	0.00050	0.996	0.00083	53.9		
0.00034	59.0	0.00058	0.994				

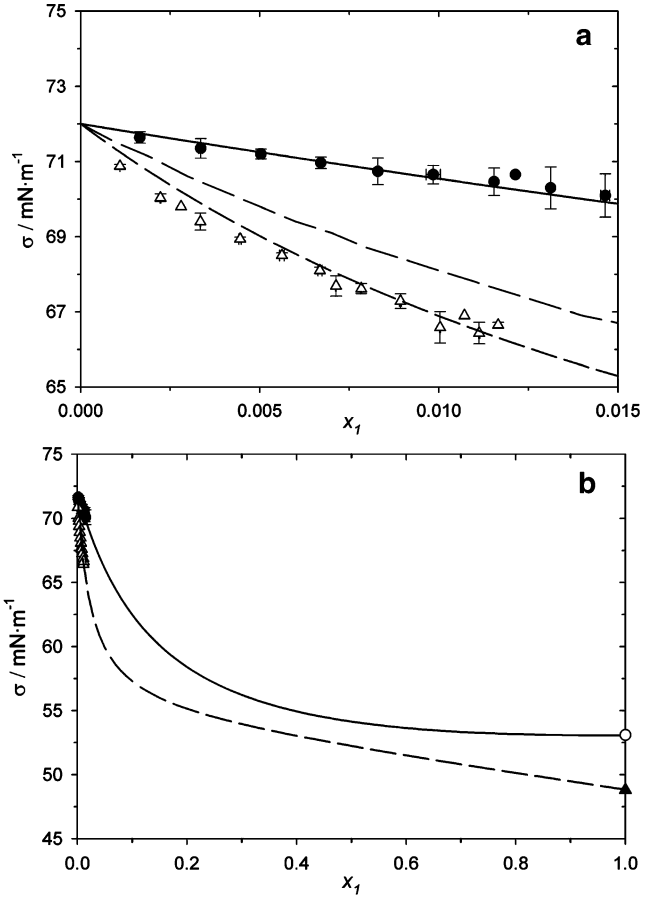

Figure 1. Measured and modeled surface tensions (σ) as a function of the acid mole fraction (x_1): ●, oxalic acid; △, succinic acid; solid line, eq 3 for oxalic acid; dashed line, eq 3 for succinic acid; gray dashed line, succinic acid.[21] Surface tension at x_1 = 1, eq 1. The error bars are standard deviations of points grouped together.

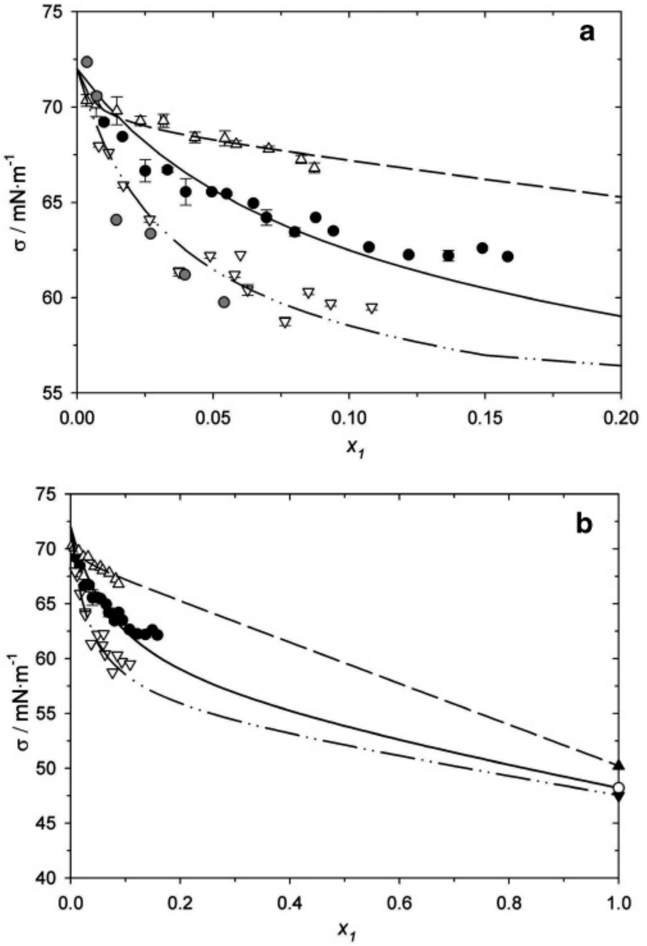

Figure 2. Measured and modeled surface tensions (σ) as a function of the acid mole fraction (x_1): ●, malonic acid; △, malic acid; ▽, maleic acid; solid, dashed, and dash−dot-dash lines, eq 3 for malonic, malic, and maleic acid, respectively; gray filled circle, malonic acid.[6] Surface tension at x_1 = 1, eq 1. The error bars are standard deviations of points grouped together.

behavior has been reported by Seidl[20] with fatty acids. The surface tensions predicted by eq 3 at 25 °C are presented in Figures 1 to 3 together with the measured values. In Figures 1a, 2a, and 3a, a direct comparison to the measured values can be made. The predicted surface tensions agree well with the measured data for all the acids. Only for malonic acid, the

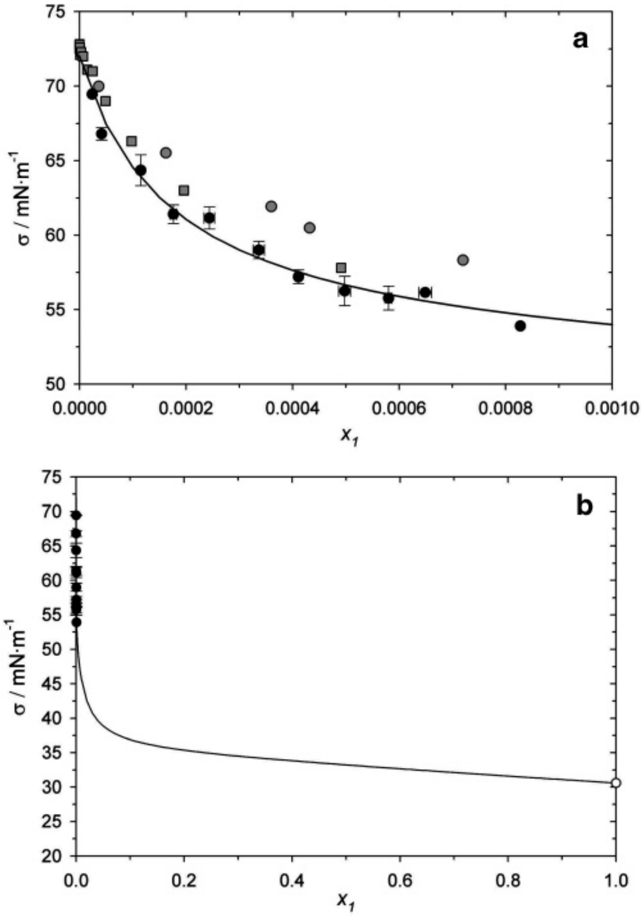

Figure 3. Measured and modeled surface tensions (σ) as a function of the acid mole fraction (x_1): ●, *cis*-pinonic acid; solid line, eq 3; gray filled circle, ref 6; gary filled square, ref 13. Surface tension at $x_1 = 1$, eq 1. The error bars are standard deviations of points grouped together.

surface tensions are slightly underestimated by the model at the highest measured mole fractions. This is due to applying the fitting outside the measurable range. Figures 1b, 2b, and 3b present the fitting for the whole mole fraction range from zero to one. These data are especially useful for model calculations for particle formation and growth, where the data outside the solubility range is more applicable. The surface tensions predicted by eq 3 seem reasonable for all the measured acids.

The results of the temperature dependent surface tension measurements are presented in Table 4 and in Figure 4. Also the surface tensions estimated by eq 3 are presented. It can be seen that the temperature dependencies of all the measurements are linear. They have approximately the same slope, regardless of the mole fraction they were measured at. For pure water, the slope is slightly steeper.[16] The difference increases with decreasing surface tension at constant acid mole fractions. The measured surface tensions and those estimated by eq 3 are close together for malic-, oxalic- and succinic acid as well as for maleic acid at $x_i = 0.012$. However, eq 3 overestimates the temperature-dependent surface tensions of malonic acid and underestimates the surface tensions of *cis*-pinonic acid and maleic acid at $x_i = 0.06$. The surface tensions estimated by eq 3 have very nearly the same temperature dependency as pure water. This means that the experimental values and eq 3 have slightly different slopes. The agreement is worst with *cis*-pinonic acid and maleic acid at $x_i = 0.06$. This is likely to be due to the uncertainties in the temperature measurements as discussed in the experimental methods or because eq 1 describing the surface tension of pure acid assumes supercooled liquid.

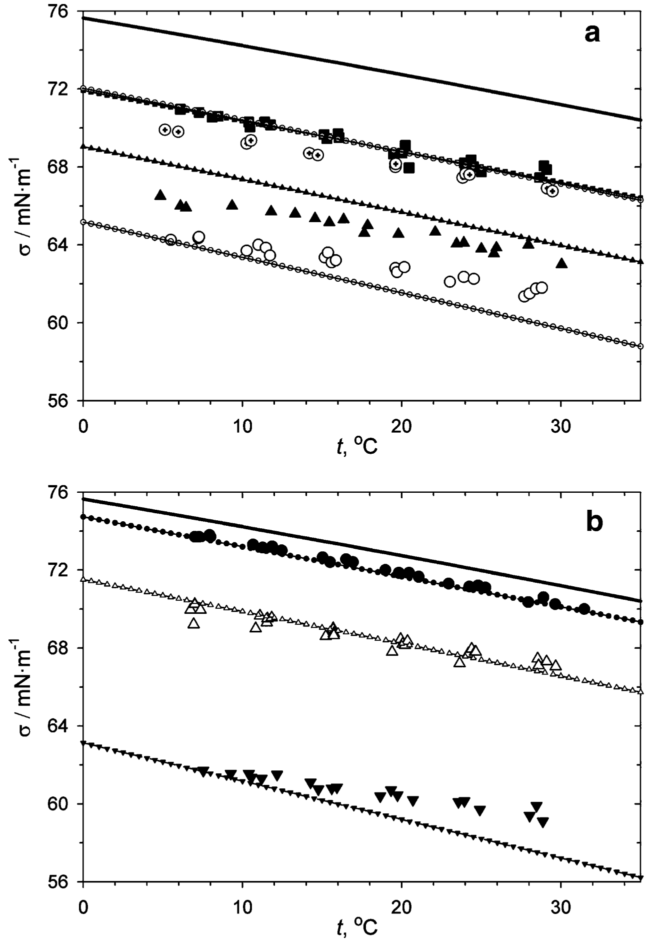

Figure 4. Measured surface tensions (σ) as a function of temperature (t). (a) ▲, malonic acid, $x_1 = 0.06$; ○, maleic acid, $x_1 = 0.06$; ⊕, maleic acid, $x_1 = 0.012$; ■, malic acid, $x_1 = 0.06$. (b) ●, oxalic acid, $x_1 = 0.0072$; △, succinic acid, $x_1 = 0.0072$; ▼, *cis*-pinonic acid, $x_1 = 0.00035$. (Both panels) solid line, water;[16] symboled lines, eq 3.

The surface tensions of some of the substances in this study have also been measured before. For comparison, the measurements by Shulman et al.[6] for malonic acid + water in Figure 2 and *cis*-pinonic acid + water in Figure 3, measurements by Tuckermann and Cammenga[13] for *cis*-pinonic acid + water in Figure 3, and a polynomial fit by Henning et al.[21] for succinic acid + water in Figure 1 are presented. Measurements by Shulman et al. for malonic acid are at a maximum 10 % lower than the results presented here. However, malonic acid is a saturated, straight-chained dicarboxylic acid with a carbon chain length between oxalic acid and succinic acid. It is expected that at the same mole fractions, the ability of malonic acid to lower the surface tension would be between that of oxalic- and succinic acid. Therefore, the sharp decrease of surface tension measured by Shulman et al. at $x_1 = 0.02$ for malonic acid seems unlikely. The surface tensions of *cis*-pinonic acid measured by Shulman et al. are about 5 % higher than the surface tensions presented here. The surface tensions of *cis*-pinonic acid measured by Tuckermann and Cammenga are also slightly higher than our result, however the difference is less than 3 %. The measurements by Tuckermann and Cammenga are at 20 °C. This can explain about 1 % of the difference. The fitting equation by Henning et al. gives about 2 % higher values than those measured by us. This is close to the experimental error estimated for our measurements.

Densities. Densities of the aqueous acid solutions were measured at room temperature. The measured densities are

Table 4. Surface Tensions (σ) of Organic Acids as a Function of Temperature (T)

T/K	σ/mN·m^{-1}	T/K	σ/mN·m^{-1}	T/K	σ/mN·m^{-1}	T/K	σ/mN·m^{-1}
Oxalic Acid, $x_1 = 0.00716$		Malonic Acid, $x_1 = 0.06$		Succinic Acid, $x_1 = 0.00716$		Malic Acid, $x_1 = 0.06$	
280.2	73.7	278.1	66.5	279.9	70.0	279.3	71.0
280.5	73.7	279.3	66.0	280.1	69.2	280.5	70.8
281.1	73.8	279.7	65.9	280.2	70.3	281.3	70.6
281.2	73.7	282.6	66.0	280.6	70.0	281.7	70.6
283.9	73.3	285.0	65.7	284.0	69.0	283.6	70.3
284.5	73.2	286.5	65.6	284.3	69.7	283.7	70.1
285.1	73.2	287.8	65.4	284.7	69.3	284.6	70.3
285.7	73.0	288.7	65.2	284.8	69.5	285.0	70.2
288.2	72.7	289.6	65.3	285.0	69.6	288.3	69.7
288.7	72.4	290.9	64.6	288.4	68.6	288.5	69.5
289.7	72.6	291.1	65.0	288.9	69.0	289.2	69.7
290.1	72.4	293.0	64.6	288.9	69.0	289.3	69.5
292.2	72.0	295.3	64.7	288.9	68.8	292.7	68.7
293.0	71.9	296.7	64.1	288.9	68.7	293.2	68.7
293.7	71.9	297.1	64.1	292.6	67.8	293.4	69.1
294.3	71.7	298.2	63.8	293.1	68.5	293.7	68.0
296.2	71.3	299.0	63.6	293.3	68.2	297.1	68.2
297.5	71.2	299.1	63.9	293.4	68.2	297.2	67.9
298.0	71.2	301.2	64.0	293.6	68.4	297.6	68.4
298.5	71.1	303.3	63.0	296.8	67.2	297.7	68.0
301.2	70.4			297.4	67.7	298.2	67.8
302.1	70.6			297.6	68.0	301.9	67.5
302.8	70.3			297.8	67.8	302.1	68.1
304.7	70.0			297.8	67.8	302.3	67.9
				297.9	67.8		
				301.7	67.5		
				301.8	67.1		
				302.3	67.3		
				302.9	67.1		
Maleic Acid, $x_1 = 0.06$		Maleic Acid, $x_1 = 0.012$		*cis*-Pinonic Acid, $x_1 = 0.00035$			
278.7	64.3	278.3	69.9	280.7	61.7		
280.4	64.4	279.2	69.8	282.5	61.6		
280.5	64.4	283.5	69.2	283.6	61.6		
283.5	63.7	283.7	69.4	283.8	61.4		
284.2	64.0	287.4	68.7	284.4	61.3		
284.7	63.9	287.9	68.6	285.4	61.5		
284.9	63.5	292.8	68.0	287.5	61.1		
288.4	63.4	292.8	68.2	288.0	60.8		
288.6	63.6	292.8	68.2	288.8	60.8		
288.8	63.1	297.0	67.5	289.1	60.9		
289.1	63.2	297.2	67.7	291.9	60.4		
292.8	62.8	297.5	67.6	292.5	60.7		
292.9	62.6	302.3	66.9	292.9	60.5		
293.4	62.9	302.7	66.8	293.9	60.2		
296.2	62.1			296.8	60.1		
297.1	62.4			297.1	60.2		
297.7	62.3			298.1	59.7		
300.9	61.4			301.2	59.4		
301.2	61.5			301.7	59.9		
301.6	61.8			302.1	59.1		
302.0	61.8						

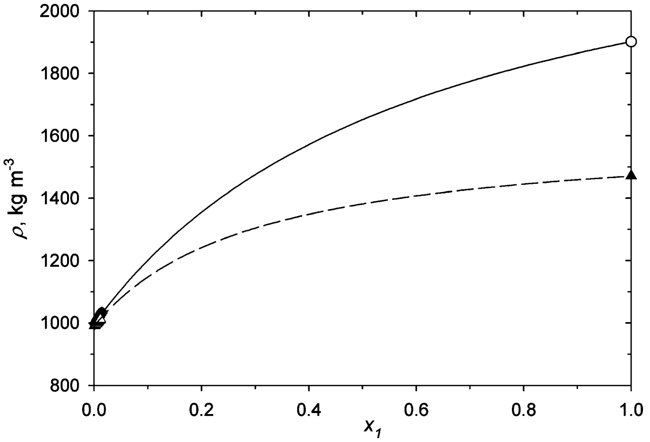

Figure 5. Measured densities (ρ) as a function of the acid mole fraction (x_1): ●, oxalic acid; △, succinic acid; solid line, eq 4 for oxalic acid; dashed line, eq 4 for succinic acid. Density at $x_1 = 1$, Yen−Woods method.[25]

presented in Table 3. The acids increase the density of pure water. The solubility of *cis*-pinonic acid is so low that it does not affect the density of the solution over the measured mole fraction range. Malic acid and oxalic acid change the density of pure water most effectively. However, due to its high solubility, malonic acid changes the density of pure water most. In a manner similar to the surface tension measurements, an equation covering the whole mole fraction range was fitted to the measurements. Assuming an ideal solution, density can be expressed as[22]

$$\frac{1}{\rho} = \frac{GM_1x_1}{\rho_1[M_1x_1 + M_2(1 - x_1)]} + \frac{HM_2(1 - x_1)}{\rho_2[M_1x_1 + M_2(1 - x_1)]} \quad (4)$$

In eq 4, M is molecular weight, x is the mole fraction, G and H are fitting parameters, and subscripts 1 and 2 denote to pure acid and water, respectively. The density of pure water as reported by Kell[23] and Pruppacher and Klett[24] was used. The densities for the pure acids were obtained with the Yen−Woods method.[25] The fitting parameters for each acid are presented in Table 2. *cis*-Pinonic acid was not fitted because of its low solubility. The fittings for the other acids agree very well with the measured values. An example of the density curves covering the whole mole fraction range is presented in Figure 5 for oxalic acid + water and succinic acid + water.

Conclusions

We have measured the surface tensions of oxalic, malonic, succinic, maleic, malic, and *cis*-pinonic acids as a function of the acid mole fraction and temperature. Densities were also measured at room temperature as a function of the acid mole fraction. All the acids lower the surface tension of pure water. *cis*-Pinonic acid, which is the least water-soluble acid in this study, lowers the surface tension most effectively but has no significant effect on density. It is possible that *cis*-pinonic acid behaves like some other nonsoluble, long-chained organic compounds[20] and forms a surface film at the air−water interface.

The surface tensions were fitted using an equation presented by Chunxi et al.[18] Densities were also fitted with a thermodynamically consistent function. The fitted functions for both the surface tension and density were extrapolated to cover the whole mole fraction range of an aqueous acid solution. The surface tensions and densities given by the fitted functions agree well with the measured values, and the estimations beyond the solubility limits seem very reasonable. This kind of estimation provides an easy to use parametrization based on experimental data, which is especially valuable in atmospheric model calculations of particle formation and growth.

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