



Surface tensions of solutions containing dicarboxylic acid mixtures



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HIGHLIGHTS

- Surface tension of dicarboxylic acid mixture was measured using Wilhelmy plate method.
- Surface tension of dicarboxylic acid mixture follows the most surface-active one.
- Modified Szyszkowski equation systematically overestimates the surface tensions.
- Henning's model systematically overestimates the surface tensions.
- The critical supersaturation ratio is reduced by adding dicarboxylic acids.

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ABSTRACT

Organic solutes tend to lower the surface tension of cloud condensation nuclei, allowing them to more readily activate. The surface tension of various dicarboxylic acid aerosol mixtures was measured at 20 °C using the Wilhelmy plate method. At lower concentrations, the surface tension of a solution with equimolar mixtures of dicarboxylic acids closely followed that of a solution with the most surface-active organic component alone. Measurements of surface tension for these mixtures were lower than predictions using Henning's model and the modified Szyszkowski equation, by ~1–2%. The calculated maximum surface excess (Γ_{\max}) and inverse Langmuir adsorption coefficient (β) from the modified Szyszkowski equation were both larger than measured values for 6 of the 7 mixtures tested. Accounting for the reduction in surface tension in the Köhler equation reduced the critical saturation ratio for these multi-component mixtures – changes were negligible for dry diameters of 0.1 and 0.5 μm , but a reduction from 1.0068 to 1.0063 was seen for the 4-dicarboxylic acid mixture with a dry diameter of 0.05 μm .

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1. Introduction

According to Köhler theory (Köhler, 1936), surface tension affects the formation and properties of clouds. The critical supersaturation required for activation of an aerosol into a cloud droplet is reduced when the surface tension decreases. Previous studies have reported that the presence of organic compounds in atmospheric aerosols lowers surface tension and critical supersaturation ratios for cloud droplets (e.g., Facchini et al., 1999; Asa-Awuku et al., 2008; George et al., 2009; Aumann et al., 2010). As a result, a larger number of smaller-sized droplets is created. This contributes to the indirect effect of aerosols on climate change by increasing the cloud albedo (Twomey, 1974, 1977) and extending

the cloud's lifetime (e.g., IPCC, 2007; Kanakidou et al., 2005; Novakov and Penner, 1993).

Organic compounds account for 20–90% of the total fine particle mass in the troposphere (e.g., Andreae and Rosenfeld, 2008; Kanakidou et al., 2005; Putaud et al., 2004). In addition, organic compounds emitted from anthropogenic and natural sources such as biomass burning are predicted to increase in the future (Andreae and Rosenfeld, 2008; Wagnener et al., 2012). Among the organic components, dicarboxylic acids have been frequently measured (e.g., Sun and Ariya, 2006); oxalic, malonic and succinic acids are three of the most prevalent dicarboxylic acids in aerosols (Braban et al., 2003; Sun and Ariya, 2006). Due to their abundance in the atmosphere and relatively high solubility in water, a better understanding is needed regarding the effect of dicarboxylic acids on aerosol surface tension.

Previous studies have measured surface tensions for a wide variety of single-component solutions. Inorganic salts have been reported to increase the surface tension of aqueous solutions by

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many researchers (e.g., Tuckermann, 2007; Weissenborn and Pugh, 1996; Abramzon and Gaukhberg, 1993). Various organic species, on the other hand, have been shown to decrease the surface tension. Tuckermann (2007) tabulated the surface tension data for pure organic solutions available in the literature. Aumann et al. (2010) also measured the surface tension for a large number of pure organic solutions including saccharides, dicarboxylic acids, aromatic polycarboxylic acids, alkanolic acid salts, and humic substances. Hyvärinen et al. (2006) studied the surface tension of dicarboxylic acid and cis-pinonic acid solutions as a function of temperature.

The surface tension of multi-component solutions also has been examined in previous studies. Tuckermann (2007) measured the surface tension of aqueous solutions containing an organic component (cis-pinonic acid) and an inorganic salt such as sodium chloride. The author observed that the effect of inorganic salt on the overall surface tension depends on the concentration of cis-pinonic acid in the solution. Other experiments on multi-component solutions have been carried out by Abramzon and Gaukhberg (1993), Shulman et al. (1996), Li et al. (1998), Fainerman et al. (2002), Kiss et al. (2005), Henning et al. (2005), Topping et al. (2006), Prisle et al. (2011), and Lee and Hildemann (2013).

A common approach for predicting the surface tension of aqueous solutions containing mixed water soluble organic compounds is to use a linear combination of the surface tensions for the individual components (Tuckermann and Cammenga, 2004; Henning et al., 2005). To combine surface tensions, Tuckermann used a weighted sum based on concentrations of the individual components, while Henning used a weighted sum based on a carbon content ratio. However, there are still relatively few experimental studies on the surface tension of organic mixture solutions. Even though real atmospheric samples are composed of complex mixtures of organics, the interactions between species in multi-component aqueous solutions are poorly understood.

In this study, the surface tension of aqueous solutions containing dicarboxylic acid mixtures was measured to examine the effect of organic mixtures on the overall surface tension. The surface tension of various types of dicarboxylic acid mixtures containing two, three or four components (e.g., malonic/glutaric acid mixtures, oxalic/malonic/succinic acid mixtures) was measured at 20 °C based on the Wilhelmy plate method. Our surface tension measurements were fitted to the Szyszkowski equation and compared with the predictions made using the modified Szyszkowski equation and Henning's model (Henning et al., 2005). In addition, the Köhler equation was used to analyze the effect of the surface tension reduction on the critical saturation ratio.

2. Experimental procedures

2.1. Materials

The properties of the dicarboxylic acids tested in this study are listed in Table 1, including the chemical formula, molecular mass (g/

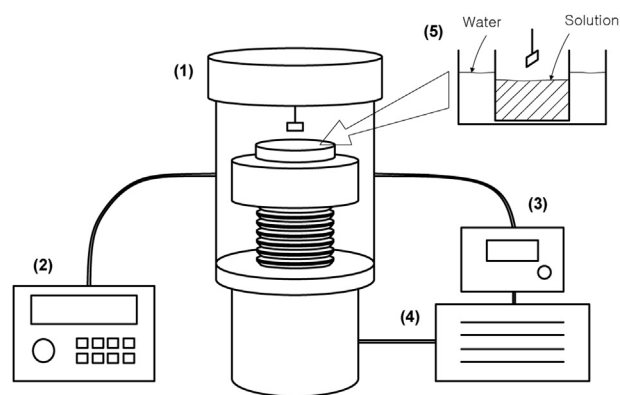


Fig. 1. Schematic of surface tension measurement apparatus. This drawing shows the interconnections between: (1) a tensiometer; (2) a programming monitor; (3) a thermostat regulator; (4) a refrigerated chiller; and (5) a double boiler system.

mol), density (g/cm^3), solubility ($\text{g}/100 \text{ g}$ of water), and manufacturer information for each of these water soluble compounds.

2.2. Surface tension measurements

To measure the surface tension of a solution, methods used in previous studies have included the Du Noüy ring method (Henning et al., 2005; Tuckermann, 2007), the pendant drop method (Svenningsson et al., 2006; Asa-Awuku et al., 2008), and the Wilhelmy plate method (Hyvärinen et al., 2006; Aumann et al., 2010). In this study, a thermostated tensiometer (Krüss K11, Germany), based on the Wilhelmy plate method, is used to measure the surface tensions of organic solutions. A thin, small plate made of platinum, which hangs on the balance, can measure the equilibrium surface tension of the aqueous solution at the air-liquid interface. Fig. 1 shows a schematic of the tensiometer apparatus.

The solutes were each weighed using a digital balance with an uncertainty of $\pm 0.01 \text{ g}$ (less than 1% of the total mass). Thus, the uncertainty in solute concentration was less than 1%. An aqueous mixed organic solution was prepared using Milli-Q purified water (18.2 M) and placed on the insulated metal holder jacket inside of the tensiometer. The temperature of this metal holder was controlled by a refrigerated chiller (Cole Parmer EW-01283-40, USA) ((3) in Fig. 1) and a programmable bath (Cole Parmer EW-12107-20, USA) ((4) in Fig. 1). The target temperature, 20 °C with an uncertainty of $\pm 0.1 \text{ °C}$ in this study, was maintained for at least 30 min to reach equilibrium.

When the organic solution at target temperature was ready, a small plate was rinsed by pure water (Milli-Q, 18.2 M) and acetone several times and then dried with flames to remove all residual chemicals on its surface. After the cleaning steps, the surface tension of the aqueous solution was measured by submerging a small platinum plate several times. During this process, the temperature of plate equalized with the temperature of the solution, and the surface tension data stabilized. Only the stabilized data were used.

Table 1
Chemical properties of organic compounds.

Compound name	Chemical formula	Molar mass (g/mol)	Density (g/cm^3)	Solubility (g/100 g) at 25 °C	Manufacturer
Oxalic acid	$\text{C}_2\text{H}_2\text{O}_4$ (HOOC–COOH)	90.03	1.900 ^a	12 ^b	Sigma–Aldrich
Malonic acid	$\text{C}_3\text{H}_4\text{O}_4$ (HOOC–CH ₂ –COOH)	104.06	1.619 ^a	161 ^b	Alfa Aesar
Succinic acid	$\text{C}_4\text{H}_6\text{O}_4$ (HOOC–(CH ₂) ₂ –COOH)	118.09	1.572 ^a	8.8 ^b	Sigma–Aldrich
Glutaric acid	$\text{C}_5\text{H}_8\text{O}_4$ (HOOC–(CH ₂) ₃ –COOH)	132.12	1.429 ^a	116 ^b	Alfa Aesar

^a Lide (2009).

^b Summarized in Saxena and Hildemann (1996).

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