TERNARY MIXTURE OF SODIUM CHLORIDE, SUCCINIC ACID AND WATER; SURFACE TENSION AND ITS INFLUENCE ON CLOUD DROPLET ACTIVATION

J. Vanhanen[1], A.-P. Hyvärinen[1], T. Anttila[1], Y. Viisanen[1] and H. Lihavainen[1]

[1]Finnish Meteorological Institute, Erik Palmènin aukio 1, 00560, Helsinki, Finland

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1. INTRODUCTION

Indirect effect of aerosol particles to the atmosphere (the cloud albedo effect) is currently the most uncertain piece in the climate change puzzle (IPCC 2007). In order to understand quantitatively how aerosols and clouds interact, the physico-chemical properties of aerosols have to be known. As the atmospheric aerosols have highly heterogeneous properties and there are only limited set of measurements characterizing them, these properties have to be treated in approximative manner in climate models. For example surface tension of pure water is often used (Anttila *et al.* 2002).

It is known that a large fraction of aerosol particles is inorganic salts (Dusek *et al.* 2006; McFiggans *et al.* 2005). Owing to their hygroscopicity, salt particles act as efficient cloud condensation nuclei (CCN). In addition of inorganic salts, an extensive number of both water-soluble and water-insoluble organic acids are present in the aerosol phase (Legrand *et al.* 2007). Organic acids are often surface active. According to Köhler theory (Köhler 1936), a decrease in surface tension induces a decrease in the critical supersaturation of a droplet. This means that organic acids can enhance the cloud droplet activation of mixed particles by decreasing the surface tension of the droplet (Cruz and Pandis, 1997, 1998; Li *et al.* 1998).

There are only a few extensive data sets on surface tensions of ternary mixtures of atmospheric relevance. To this end, we studied the surface tension of ternary solution of sodium chloride, succinic acid and water as a function of both concentration and temperature. The measured surface tensions were used as an input to an adiabatic air parcel model (Anttila *et al.* 2002) to study the effect of the surface tension on cloud droplet activation.

2. MATERIALS AND METHODS

The surface tension was measured using a capillary rise technique (figure 1). The sample was placed in a small glass in the bottom of a double-walled glass. The temperature of the glass was controlled by circulating thermostatically controlled liquid between the walls (Lauda RC6 CS).

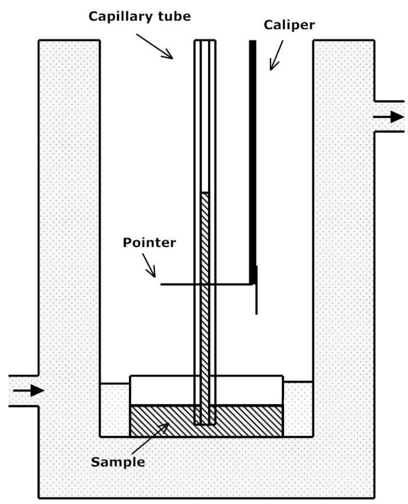

Figure 1. Experimental setup

The samples were made of pure substances with purity of 99 % or better. Both sodium chloride and succinic acid were dried before weighing in an oven at temperature of about 100 ^{o}C to evaporate all the volatile impurities. Before every measurement the capillary tubes were cleaned using 96% sulfuric acid and purified water (Milli-Q).

The height of the liquid in the capillary tube was measured using a slide caliper modified to this purpose. Accuracy of the caliper is ±0.02 mm. The measurements were performed inside temperature range 283.15 K to 303.15 K. The meniscus was allowed to both rise and descent by altering the pressure in the tube. Uncertainty of the surface tension measurement was estimated to be less than 1 %.

3. SURFACE TENSION

Surface tension of the ternary solution of sodium chloride, succinic acid and water was measured as a function of mixture composition and temperature. The range of concentrations covered by measurements was limited by their solubilities. The maximum mole fractions used were 0.0075 and 0.06 for succinic acid and sodium chloride respectively.

In figure 2 the surface tension measurements of aqueous succinic acid is presented and compared to the previous measurements made with the Wilhelmy-plate method by Hyvärinen *et al.* 2006. It can be seen that succinic acid decreases the surface tension of the solution already at quite small mole fractions. Results agree well with the previous measurements done using a different method. Sodium chloride was found to increase surface tension linearly as a function of concentration.

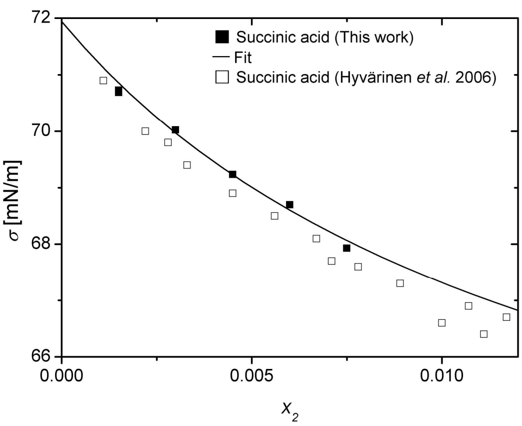

Figure 2. Surface tensions of aqueous succinic acid as a function of the mole fraction of succinic acid (x_2) at 25^{o}C.

In figure 3 the surface tension of the ternary solution is presented as a function of temperature for four different mole fractions of succinic acid. The sodium chloride mole fraction is 0.02. Surface tension of the solution decreased with increasing temperature as expected. The behaviour is similar also with other concentrations of sodium chloride. The gradient of surface tension with respect to the temperature gets lower with increasing concentrations of both solvents.

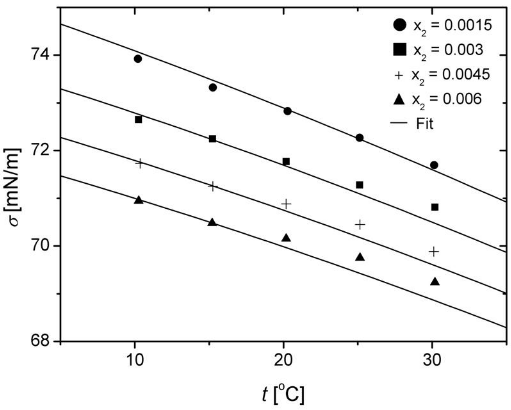

Figure 3. Surface tension of ternary solution of sodium chloride, succinic acid and water as a function of temperature. Mole fraction of sodium chloride is kept constant (x_3 = 0.02).

In figure 4 the surface tension of the ternary solution is presented as a function of mole fractions of succinic acid and sodium chloride at 25^{o}C. The decrease of the surface tension as a function of succinic acid mole fraction is steeper for solutions with larger amount of the salt. This indicates that succinic acid, as a surface active compound, tends to fill the surface of the ternary solution. It has been found in previous studies that in some cases inorganic salts can even enhance the surface tension lowering of organic acids (Tuckermann 2007; Kiss *et al.* 2005).

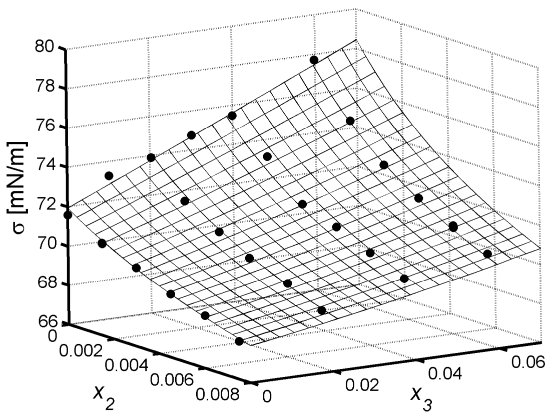

Figure 4. Surface tension of the ternary mixture as a function of mole fractions of succinic (x_2) acid and sodium chloride (x_3) at 25^{o}C.

To make the measurement results useful for numerical models, they need to be extrapolated to a larger concentration and temperature range. To this end, a function by Chunxi *et al.* (2000) was fitted to the data. This way we got a surface tension parameterization which can be used beyond solubility limits. Fit can be seen in the figures as a solid line.

5. CLOUD DROPLET ACTIVATION

To see if surface tension has an effect on cloud droplet activation, we compared results from cloud model simulations that used two different surface tensions in *S*: that of pure water and that predicted by the developed surface tension parameterization.

The aerosol size distribution used in the simulations represents a typical aerosol size distribution measured in marine environment (Heintzenberg *et al.* 2000). Succinic acid is treated as a completely soluble compound despite of its solubility limit (88 g/l; Saxena *et al.* 1996). Previous studies have shown that the solubility of a slightly soluble compound has an effect only when there is no or very little of sodium chloride in the particle (Bilde *et al.* 2004). Also, particles have usually undergone different kinds of humidity conditions in the atmosphere. This means that the solution can be supersaturated with respect to succinic acid, and the assumption of complete solubility is sensible.

Cloud model simulations were made using three different updraft velocities; 0.1, 0.5 and 1.0 m/s. In figure 5 the ratio of the number of cloud droplets (N_a) to the total number of particles (N_i) (activated fraction) is presented as a function of the initial mass fraction of succinic acid in the aerosols. The activated fraction decreases as the mass fraction of succinic acid increases. This is because succinic acid has higher molar volume than sodium chloride and because sodium chloride is able to dissociate in water.

In figure 5, it can be seen that there is a difference in the number of cloud droplets arising from the choice of the surface tension. The difference increases with increasing mass fraction of succinic acid and with increasing updraft velocity. By using the surface tension of pure water in the cloud model the amount of activated particles is underestimated up to 8 % for aerosol size distributions containing succinic acid and overestimated up to 8 % for size distributions containing only sodium chloride. This is because succinic acid decreases the surface tension of the solution while sodium chloride increases it. When the updraft velocity of the air parcel is 1.0 m/s, the effect of surface tension can clearly be seen with particles having mass fraction of succinic acid over 40%. Mass fractions of organic compounds in atmospheric aerosol particles can easily exceed this value (Dusek *et al.* 2006). The effect of updraft velocity can be explained by a larger dry diameter of activated particles, which is due to the lower updraft velocity, and thereby lower supersaturation. This decreases the Kelvin effect, which takes into account the surface tension of the solution. This was also observed for marine aerosol size distribution previously by Nenes *et al.* (2002).

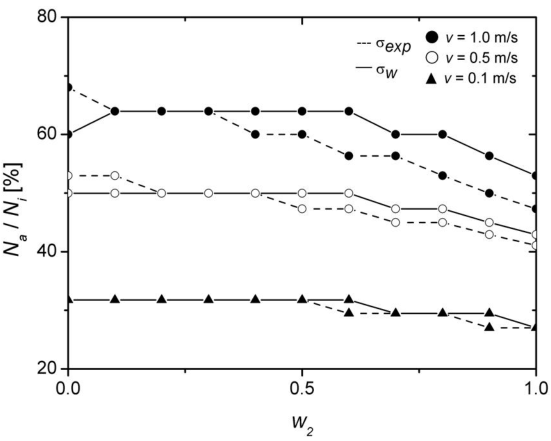

Figure 5. Activated fraction as a function of mass fraction of succinic acid (w_2). *v* is the updraft velocity, σ_w is the surface tension of pure water and σ_{exp} is the surface tension parameterization.

4. CONCLUSIONS

In this study the surface tension of ternary solution of sodium chloride, succinic acid and water was measured using the capillary rise technique. Measured surface tensions of binary solutions agreed well with literature values, confirming that the method is applicable to these solutions. Measurements were performed within the concentration range defined by the solubility limits of the solvents. To estimate the surface tension beyond these limits, an equation developed by Chunxi *et al.* (2000) was fitted to the data. As a result a parameterization of surface tension of the ternary solution was obtained over the whole concentration range. The parameterization is applicable inside temperature range of 10 to 30 ^{o}C, but it can be extrapolated beyond these limits. There are many benefits with these kinds of parameterizations. First, it gives the surface tension of ternary system as a function of both composition and temperature. Second, the parameterization is based on thermodynamics having fit parameters which can be, for example modelled. This gives many options for future research. Because the parameterization can be used beyond solubility limits, it can be also applied, for example, in numerical calculations regarding nucleation or cloud droplet formation.

To estimate the atmospheric relevance of the surface tension data, cloud droplet activation simulations were performed with particles of different composition. Three different updraft velocities (0.1, 0.5 and 1.0 m/s) were used. It was found that while sodium chloride particles act as efficient cloud condensation nuclei, succinic acid can enhance the activation further by decreasing the surface tension of the aqueous solution. By using the surface tension of pure water in the cloud model the amount of activated particles was underestimated up to 8% if the initial particles contained succinic acid. For pure sodium chloride particles it was overestimated up to 8%. Although the changes are small percent-wise, they still may have significance to the cloud radiative properties, in particular over the oceans. The marine clouds are usually clean clouds having lower number concentration of cloud droplets, which makes them especially sensitive to changes in the cloud droplet concentration (Platnic and Twomey 1994).

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