

THE CCN PROPERTIES OF 2-METHYLTETROLS AND C3-C6 POLYOLS

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1. INTRODUCTION

The contribution of atmospheric aerosols to the climate and their control of cloud droplet activation and cloud optical properties is poorly understood [Forster *et al.*, 2007]. Atmospheric observations have previously shown that organic matter are involved in cloud activation [Novakov and Penner, 1993; Liu *et al.*, 1996; Rivera-Carpio, 1996; Matsumoto *et al.*, 1997; Ishizaka and Adhikari, 2003; Moshida *et al.*, 2006; Chang *et al.*, 2007]. Organic compounds seem especially important in clean environments and were found to have a large contribution to the Cloud Condensation Nuclei (CCN) numbers in marine regions and at a continental semi-rural site [Novakov and Penner, 1993; Rivera-Carpio, 1996; Matsumoto *et al.*, 1997; Chang *et al.*, 2007]. The presence of organic compounds was also necessary to account for the CCN numbers observed in the Amazon basin [Mircea *et al.*, 2005]. A contribution of organic material to CCN could be especially critical in pristine regions where CCN numbers are limited by very low aerosol concentrations [e.g. Fitzgerald, 1991; Roberts *et al.*, 2001].

A large number of investigations have tried to identify the organic compounds that would take part in cloud droplet activation. A property that seems essential in these processes is their solubility in water, which has been shown to affect, if not CCN numbers, particles growth factors [e.g. Mircea *et al.*, 2005]. It has been shown that a significant fraction of biogenic aerosols consists of compounds of solubility comparable or even larger than those of inorganic salts such as polyols and the 2-methyltetrols, methylerythritol and methylthreitol [Claeys *et al.*, 2004; Ion *et al.*, 2005; Kourtchev *et al.*, 2005; Böge *et al.*, 2006]. These compounds were

found in clean environments [Claeys *et al.*, 2004] and fine aerosols [e.g. Kourtchev *et al.*, 2005; Böge *et al.*, 2006], which makes them good candidates for CCN in the natural atmosphere. This role could be important for both the 2-methyltetrols and the polyols at global scale. The methyltetrols are thought to be produced by the oxidation of isoprene, one of the organic gases the most emitted globally and the polyols are mainly emitted by fungi. Although the CCN properties of polyols and 2-methyltetrols are central to the understanding of cloud formation in clean environments, they have not been investigated until now. This work presents the first investigation of the CCN properties of C3 to C6 polyols and of the tetrols, methylerythritol and methylthreitol.

2. EXPERIMENTAL

The experimental approach used in this work was recently described by Kiss and Hansson, [2004] and Varga *et al.*, [2007]. For each compound or mixture studied solutions of different concentrations up to 2 M were prepared. The particle radius, r , corresponding to each concentration was calculated from the density of the pure material (CRC [1970], except for arabitol and the methyltetrols assumed to be 1480 kgm⁻³ and 1460 kgm⁻³, respectively), and adding up the volumes of aqueous solution and organic material. The osmolality of these solutions (reduction of water vapor pressure due to the solute), C_{osmol} (kg⁻¹), was measured with a KNAUER K – 7000 vapor pressure osmometer. The surface tension of each solution, σ_{sol} (mN m⁻¹), was measured with a FTÅ 125 tensiometer. The water activity, a_w , was determined from the osmolality [Kiss and Hansson, 2004].

The experimental values for a_w and σ_{sol} were then used to calculate the supersaturation, S , the excess vapor pressure necessary to activate the aerosol particle into a droplet, using the original (i.e. non-simplified) Köhler equation. The Köhler curves were thus built point by point for the different organic compounds and salt solutions. As discussed previously [Kiss and Hansson, 2004], this method is experimentally simple, accurate and has the advantage of eliminating the uncertainties contained in the simplified Köhler equation, in particular in the Van't Hoff factors. Finally, this method can be applied to particles of almost any size, the range accessible to measurements being only limited by the solubility of the compounds in the solutions of interest.

A first series of experiments determined the CCN properties of the polyols, glycerol (C3), erythritol (C4), arabitol (C5), and mannitol (C6), and the two 2-methyltetrols in water, as well as those of their analogue di-acids, malonic acid (C3), succinic acid (C4), and adipic acid (C6). Because previous studies have shown that the presence of inorganic salts could dramatically affect CCN efficiency of partly soluble organic compounds [Bilde and Svenningsson, 2004], a second series of experiments focused on the CCN properties of the polyols and 2-methyltetrols in sodium chloride and ammonium sulfate solutions.

3. RESULTS AND DISCUSSION

In order to present the measurements made in this work Köhler curves were determined by the method explained in the previous section for the various organic compounds and a dry particle radius of 30 nm. For the polyols and di-acids in water these curves are shown in Figure 1, and for the 2-methyltetrols in water in Figure 2. The results obtained in this work for the organic acids, in particular the critical supersaturation (maxima of the curves), are in good agreement with earlier studies [Bilde et al., 2004, Hori et al., 2003, Giebl et al., 2002,

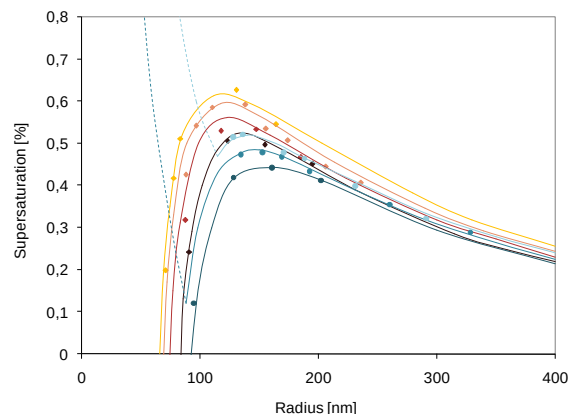


Figure 1: Köhler curves for polyol and dicarboxylic acid particles. Diamonds Polyols (glycerol: black, erythritol: red, arabitol: orange, mannitol: yellow); Circles: dicarboxylic acids (malonic acid: dark blue, succinic acid: medium blue, adipic acid: light blue).

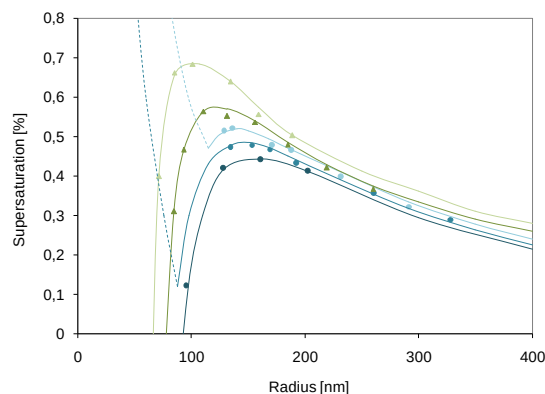


Figure 2: Köhler curves for 2-methyltetrol and dicarboxylic acid particles. Triangles: Methyltetrols (2-methylthreitol: light green, 2-methylerythritol: dark green). Other compounds as in figure 1.

Prenni et al., 2001, Corrigan et al., 1998, Cruz and Pandis, 1997], which confirms the validity of the technique and of the measurements.

Figures 1 and 2 show that the critical supersaturation for the polyols ($Sc = 0.52 - 0.62 \pm 0.02$ %) and 2-methyltetrols ($Sc = 0.57 - 0.68 \pm 0.02$ %) are slightly higher than those of the analogue di-acids ($Sc = 0.44 - 0.52$

%), but lower than for mono- and disaccharides ($Sc = 0.55 - 0.85$ %) [Rosenørn *et al.*, 2005]. Thus, in contrast to what expected, high solubility does not necessarily correspond to high CCN efficiency. It is well established that the high CCN efficiencies of sodium chloride and ammonium sulfate result from their Raoult effect, corresponding to high osmolalities. The organic compounds studied in this work had significantly lower osmolalities than the inorganic salts, especially the 2-methyltetrols. This difference reflects mostly the degree of dissociation of each compound and the corresponding concentration of solute.

The organic acids are known to have some surface tension effects that partly compensate for their low water activities and improve their CCN efficiencies [Facchini *et al.*, 1999]. In this work, the surface tension of all compounds were measured and none of the polyols displayed any significant surface tension effect, but the 2-methyltetrols displayed a small effect. These effects contributed to lower their critical supersaturation, but not enough to compete with the inorganic salts or even the organic acids.

Experiments salt solutions showed that sodium chloride strongly reduces the critical supersaturation for adipic acid compared to pure water. However, ammonium sulfate were found to have a smaller effect. For mannitol, the critical supersaturation was reduced by both salts, which suggests that mannitol is only partly soluble in water, in agreement with the moderate solubility [Saxena and Hildemann, 1996]. As with adipic acid, a smaller reduction of the critical supersaturation was observed with ammonium sulfate than with sodium chloride. By contrast, the critical supersaturation of methylthreitol was hardly affected by the presence of either salt. Assuming a solubility for this compound similar to the one of threitol [Cohen, 1983] suggests that it should be completely soluble in water, in which case no effect of salt on the Köhler curve is expected [Bilde and Svenningsson, 2004]. Interestingly, the critical supersaturation for

methylerythritol was increased by both salts. Assuming a solubility for this compound similar to the one of erythritol [Cohen, 1983] suggests that this compound should be only partly insoluble in water. However, unlike the di-acids and other polyols, the non-soluble part would be liquid, not a solid, which could form a film at the surface of the droplets and de-activate the uptake of water.

Although the results of this work show that the polyols and 2-methyltetrols would not activate cloud formation at lower supersaturation than inorganic salts or organic acids, their high solubility gives them one advantage: to activate smaller particles than less soluble compounds. For organic compounds of limited solubility, the very high critical supersaturation of the non-soluble part of the Köhler curves (dashed lines in the Figures) is an efficient barrier against the activation of small particles [Bilde and Svenningsson, 2004]. The presence of highly soluble biogenic material such as polyols, 2-methyltetrols, or sugars in aerosols could thus increase CCN numbers compared to aerosols containing only partly soluble compounds. This effect could be especially critical in pristine environments where aerosol concentrations are very low [Fitzgerald, 1991; Roberts *et al.*, 2001], which are precisely the environments where this highly soluble biogenic material is present.

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