

The Cloud Condensation Nuclei (CCN) properties of 2-methyltetrols and C3-C6 polyols from osmolality and surface tension measurements

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Received: 18 August 2008 – Published in Atmos. Chem. Phys. Discuss.: 11 September 2008

Revised: 17 November 2008 – Accepted: 14 January 2009 – Published: 6 February 2009

Abstract. A significant fraction of the organic material in aerosols is made of highly soluble compounds such as sugars (mono- and polysaccharides) and polyols such as the 2-methyltetrols, methylerythritol and methyltreitol. Because of their high solubility these compounds are considered as potentially efficient CCN material. For the 2-methyltetrols, this would have important implications for cloud formation at global scale because they are thought to be produced by the atmospheric oxidation of isoprene. To investigate this question, the complete Köhler curves for C3-C6 polyols and the 2-methyltetrols have been determined experimentally from osmolality and surface tension measurements. Contrary to what was expected, none of these compounds displayed a higher CCN efficiency than organic acids. Their Raoult terms show that this limited CCN efficiency is due to their absence of dissociation in water, this in spite of slight surface-tension effects for the 2-methyltetrols. Thus, compounds such as saccharides and polyols would not contribute more to cloud formation than other organic compounds studied so far. In particular, the presence of 2-methyltetrols in aerosols would not particularly enhance cloud formation in the atmosphere, in contrary to recently suggested.

1 Introduction

One of the most important roles of atmospheric aerosols for Earth's climate, yet still the least understood, is their control of cloud droplet activation and cloud optical properties (aerosol indirect effect) (Forster et al., 2007). While inorganic salts are considered as the most efficient cloud-forming materials, atmospheric observations have increasingly suggested the involvement of organic matter in these processes (Novakov and Penner, 1993; Liu et al., 1996; Rivera-Carpio et al., 1996; Matsumoto et al., 1997; Ishizaka and Adhikari, 2003; Moshida et al., 2006; Chang et al., 2007). Organic compounds were thus estimated to contribute to up to 63 or 80% of Cloud Condensation Nuclei (CCN) numbers in marine regions (Novakov and Penner, 1993; Rivera-Carpio et al., 1996; Matsumoto et al., 1997), and 20% at a continental semi-rural site (Chang et al., 2007). The presence of organic compounds was also found to be necessary to account for the CCN numbers in the Amazon basin (Mircea et al., 2005). A contribution of organic material to CCN could be especially important in pristine environments, such as remote marine regions or the Amazonian wet season, where CCN numbers are limited by the low aerosol concentrations (e.g. Fitzgerald, 1991; Roberts et al., 2001). Understanding cloud formation in these regions is important both as a contribution to the global atmosphere and as an observatory of the pristine atmosphere.



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Table 1. Solubility in water for the compounds discussed in this work.

	Compound	Solubility [g L ⁻¹]	Reference
Polyols:			
	Methyl threitol	8800 ^a	
	Methyl erythritol	637 ^b	
	Glycerol Threitol	infinite 8800	Saxena and Hildemann, 1996; Cohen, 1993
	Erythritol	637	Cohen, 1993
	Arabitol	1510–2110	Saxena and Hildemann, 1996
	Mannitol	216	Hu, 1998
Saccharides:			
	Fructose	4074	Washburn, 1927
	Mannose	2500	Windholtz, 1983
	Sucrose	2000	Windholtz, 1983
	Glucose	909	Windholtz, 1983
	Lactose	200	Windholtz, 1983
	Maltose	93	Washburn, 1927
Di-acids:			
	Malonic acid	1610	Saxena and Hildemann, 1996
	Succinic acid	88	Saxena and Hildemann, 1996
	Adipic acid	25	Saxena and Hildemann, 1996
Inorganic salts:			
	Ammonium Sulphate:	706	Weast, 1985
	Sodium Chloride:	357	Weast, 1985

^a Assumed identical to threitol;

^b Assumed identical to erythritol.

Some properties of organic compounds, such as their effect on the surface tension, have been clearly shown to play a critical role in cloud droplet formation (Facchini et al., 1999). The role of other molecular properties, such as their solubility in water, is less clear but generally suspected and subject to many investigations (e.g. Mircea et al., 2005). Many aerosols in the atmosphere contain significant fractions of organic compounds of solubility comparable or larger than those of inorganic salts such as sugars (mono- and polysaccharides), polyols, and the 2-methyltetrols, methylerythritol and methylthreitol (Claeys et al., 2004; Ion et al., 2005; Kourchev et al., 2005; Böge et al., 2006). This highly soluble material accounts for up to 5% of the total organic fraction of aerosols in forested (e.g. Graham et al., 2003; Decesari et al., 2006; Fuzzi et al., 2007), and marine regions (e.g. Simoneit et al., 2004). Polyols and 2-methyltetrols, in particular, were found in the fine aerosol fraction in forested and rural areas (e.g. Graham et al., 2003; Kourchev et al., 2005; Böge et al., 2006). The potential role of these 2-methyltetrols as CCN material has been strongly suggested (Silva Santos et al., 2006; Meskhidze and Nenes, 2006) and would have tremendous implications for cloud formation at global scale as these compounds are believed to be produced by isoprene, a gas globally emitted. The CCN efficiencies of saccharides have been previously studied (Rosenørn et al., 2005) and found to be lower than those of organic acids. But

the CCN efficiencies of polyols and 2-methyltetrols 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 (see molecular structures and properties in Tables 1 and 2).

2 Experimental

The experimental method used in this work is the one developed by Kiss and Hansson (2004) and Varga et al. (2007), and the readers are referred to these articles for an in-depth description. The principle is to build the Köhler curve, $S(d)$, of the compounds of interest point by point by measuring some properties of their solutions in water (or salt solutions). The Köhler curve, $S(d)$, describes the supersaturation (or excess vapor pressure) necessary to activate a particle of diameter d into a cloud droplet:

$$S(d) = \left(a_w \times \exp \frac{4\sigma_{\text{sol}} M_w}{d\rho_w RT} \right) - 1, \quad (1)$$

where a_w is the water activity, σ_{sol} (mN m⁻¹) the surface tension, M_w the molecular weight of water (18 g mol⁻¹), ρ_w the density of water (1 g cm⁻³), R the gas constant, and T temperature. In this equation, only a_w and σ_{sol} are related to the compounds studied while all other parameters are either constant or related to water. The values of a_w and σ_{sol} were

Table 2. Chemical structures and molecular properties of the compounds studied in this work.

Compound	Molecular formula	Molecular weight [g mol ⁻¹]	Density [g cm ⁻³]	Molecular structure
Polyols:				
Methyl threitol	C ₅ H ₁₂ O ₄	136.15	1.46*	
Methyl erythritol	C ₅ H ₁₂ O ₄	136.15	1.46*	
Glycerol	C ₃ H ₈ O ₃	92.11	1.261 ^(a)	
Erythritol	C ₄ H ₁₀ O ₄	122.12	1.451 ^(a)	
Arabitol	C ₅ H ₁₂ O ₅	152.15	1.48*	
Mannitol	C ₆ H ₁₄ O ₆	182.18	1.489 ^(a)	
Di-acids				
Malonic acid	C ₃ H ₄ O ₄	104.06	1.619 ^(a)	
Succinic acid	C ₄ H ₆ O ₄	118.09	1.572 ^(a)	
Adipic acid	C ₆ H ₁₀ O ₄	146.14	1.36 ^(a)	
Inorganic salts:				
Ammonium Sulphate	(NH ₄) ₂ SO ₄	132.14	1.77 ^(a)	
Sodium Chloride	NaCl	58.44	2.16 ^(a)	

* Approximate value

^(a) Weast, 1985

measured experimentally from mixtures of the compounds of interest in water or in salt solutions. To build the complete Köhler curve, each mixture was prepared for a range of different concentrations corresponding to different particle diameter, d . The concentrations of organic were varied between 0 and 2 M, and those of salt between 0 and 1 M (see details in Table 3). The curves were typically built on 5 to 10 points (shown in the Figures). The particle diameter corresponding to the solution concentration was calculated by adding up the volumes of aqueous and of organic materials, the latter assuming the density of the pure organic material (see Table 2).

The surface tension of the solutions, σ_{sol} (mN m⁻¹), was measured with a FTÅ 125 tensiometer, with overall uncertainties of $\pm 2\%$. The water activity, a_w , was determined from the osmolality of these solutions, C_{osmol} (kg⁻¹), (reduction of water vapor pressure due to the solute), according to:

$$a_w = \frac{1000}{\frac{1000}{M_w} + C_{\text{osmol}}} \quad (\text{Kiss and Hansson, 2004}), \quad (2)$$

where C_{osmol} was measured experimentally with a KNAUER K-7000 vapor pressure osmometer. This method provides a_w with an excellent accuracy compared to literature data (Kiss

Table 3. Linear parametrization of the surface tension and osmolality measurements as function of molar concentration.

Compound	Surface tension (mN m ⁻¹)	<i>r</i> ²	Osmolality (×10 ⁻³ kg ⁻¹)	<i>r</i> ² range (M)	Concentration
Water					
Glycerol	-1.8 c+71.6 (6)	0.97	965.2 c-9.1 (6)	0.99	0.05-2.01
Erythritol	-2.5 c+72.0 (6)	0.89	1107.9 c-14.0 (6)	1.00	0.05-1.00
Arabitol	-3.5 c+71.5 (8)	0.64	1018.5 c+3.2 (8)	1.00	0.02-0.40
Mannitol	-3.2 c+71.7 (6)	0.93	1072.4 c-9.3 (6)	1.00	0.05-1.00
Methylerythritol	-14.3 c+70.4 (12)	0.97	955.1 c-44.8 (12)	0.99	0.02-1.87
Methylthreitol	-16.1 c+72.3 (7)	0.96	610.2 c-19.2 (7)	0.97	0.05-1.20
Malonic acid	-4.6 c+70.8 (6)	0.95	978.6 c+19.5 (6)	1.00	0.05-2.02
Succinic acid	-19.4 c+72.1 (6)	0.95	1018.1 c+9.8 (6)	1.00	0.01-0.15
Adipic acid	-46.8 c+70.5 (6)	0.98	1016 c+8.3 (6)	1.00	0.01-0.12
Sodium Chloride	-2.4 c+71.3 (8)	0.62	1800 c-6.5 (8)	1.00	0.01-1.00
Ammonium sulphate	-2.7 c+70.8 (9)	0.93	1946 c+15.3 (9)	1.00	0.01-1.00
Ammonium Sulphate (17% wt/wt)					
Mannitol	-4.0 c+71.6 (9)	0.91	1322.1 c-18.4 (9)	1.00	0.03-2.07
Methylerythritol	-15.1 c+73.4 (9)	1.00	941.8 c-103.8 (9)	0.95	0.05-1.53
Methylthreitol	-14.9 c+73.5 (9)	1.00	907.7 c-67.9 (9)	0.97	0.04-1.31
Adipic acid	-40.5 c+71.1 (6)	0.98	1011.2 c-11.9 (6)	1.00	0.02-0.07
Sodium Chloride (17% wt/wt)					
Mannitol	-2.7 c+70.9 (9)	0.95	1655.7 c-19.7 (9)	1.00	0.01-1.05
Methylerythritol	-14.2 c+73.3 (9)	0.98	1071.8 c-95.0 (9)	0.96	0.05-1.44
Methylthreitol	-13.0 c+73.7 (9)	0.97	966.2 c-95.8 (9)	0.97	0.05-1.42
Adipic acid	-25.7 c+69.4 (6)	0.95	1019.9 c+36.9 (6)	0.92	0.04-0.13

and Hansson, 2004) and less than 2% of errors for up to 1.5 mol kg⁻¹ of solute. Uncertainties on these measurements were between ±4% (intermediate concentrations of organics) to ±12% for very dilute and very high concentrations of organics. The uncertainties on C_{osmol} and σ_{sol} resulted in uncertainties between ±4% and ±7% on $S(d)$. The critical supersaturations, S_c , had the lowest uncertainties, ±4%, because they corresponded to intermediate organic concentrations, where the uncertainties on C_{osmol} were minimal.

Note that this method employs the original Köhler Eq. (1), where the use of Van't Hoff factors is replaced by experimental values of the osmolality. Not only this avoids assumptions in the determination of these factors but also takes into account intermolecular and electrostatic effects between the molecules of solute that the expression with Van't Hoff factors does not. Kiss and Hansson (2004) thus showed that using osmolality instead of Van't Hoff factors improved by 40% the Raoult term for sulfuric acid, and by about 15% its critical supersaturation. Similar (but smaller) effects were also shown for NaCl and CaCl₂ (Kiss and Hansson, 2004).

A first series of experiments focused on determining the Köhler curves for the pure organic compounds, glycerol (C3), erythritol (C4), arabitol (C5), mannitol (C6), their diacid analogs, malonic acid (C3), succinic acid (C4), adipic

acid (C6), and the two 2-methyltetrols, from their solutions in water (Tables 1 and 2). All the Köhler curves presented in this work, and all critical supersaturation values discussed, have been determined for a dry particle diameter of 60 nm.

Because organic material is often mixed with inorganic salts in aerosols, which can affect their Köhler curves (Bilde and Svenningsson, 2004), a second series of experiments focused on the determination of the Köhler curves for the organic compounds mixed with sodium chloride and ammonium sulfate. All these solutions had a composition of 17% wt in salt. Note that these Köhler curves were determined only for the range of concentrations where the organic compounds were soluble.

Chemicals. 2-methylerythritol and 2-methylthreitol were custom synthesized by InnoChemie GmbH, Germany. The synthesis proceeded first to Compound 1 (Fig. 1), which was isolated in >98% purity. After hydrolysis, benzaldehyde 2 was removed by repeated azeotropic distillation with water to furnish 3 in nearly quantitative yield containing ~10% of water. Residual water was removed by repeated azeotropic distillation using ethanol and the final product was dried under reduced pressure to remove ethanol. The estimated purity of 2-methylerythritol and 2-methylthreitol was >95%.

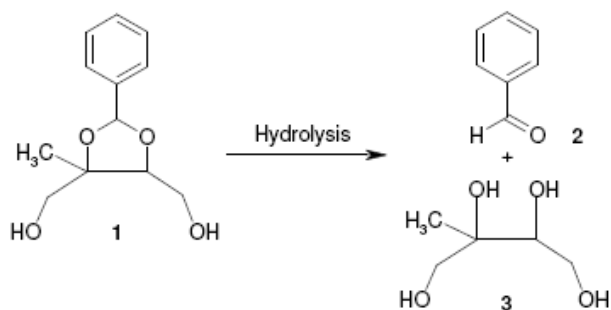


Fig. 1. Details of the molecular structures of the intermediates in the synthesis of the methyltetrols (courtesy of Innochemie GmbH).

All other compounds were commercially available from the manufacturers: Malonic acid (Aldrich, purity 99%), succinic acid (Aldrich, $\geq 99\%$), adipic acid (Aldrich, purity 99%), glycerol (Aldrich, purity $\geq 99.5\%$), erythritol (Aldrich, $\geq 99\%$), arabitol (Aldrich, purity $\geq 99\%$), mannitol (Aldrich, purity 98%), sodium chloride (Aldrich, purity $\geq 99\%$), ammonium sulfate (Aldrich, purity $\geq 99.5\%$).

3 Results and discussion

3.1 Organic/water mixtures

The measurements of C_{osmol} and σ_{sol} as function of the organic concentration, $c(\text{M})$, made in this work are summarized in Table 3 as their best fit to linear expressions over the ranges of concentration studied.

The Köhler curves for the polyols and di-acids are shown in Fig. 2, and for the 2-methyltetrols, in Fig. 3, all for a dry diameter of 60 nm. Table 4 compares the critical supersaturations, S_c , obtained in this work for malonic, succinic, and adipic acid and a dry diameter of 100 nm, with those obtained with on-line techniques (HTDMA and CCN counters), and theoretical values. For malonic and succinic acids, the results of the different techniques are in excellent agreement, showing the validity of the method presented in this work, even for these surface-active compounds. Previous on-line determinations of S_c for adipic acid were rather scattered. However, the value determined by the method presented in this work is the closest to the theoretical one, further confirming the validity of this method.

The Köhler curves obtained for the polyols ($S_c=0.5\text{--}0.63\pm 0.02\%$, Fig. 2) and the 2-methyltetrols ($S_c=0.57\text{--}0.68\pm 0.02\%$, Fig. 3) showed that the critical supersaturations of these compounds were all higher than those of their analogue di-acids ($S_c=0.44\text{--}0.52\%$) (all curves and S_c values for a dry diameter of 60 nm). This demonstrates that, in contrast to what was expected, a high solubility does not necessarily imply a high CCN efficiency. These results are in line with the low CCN efficiencies previously measured for

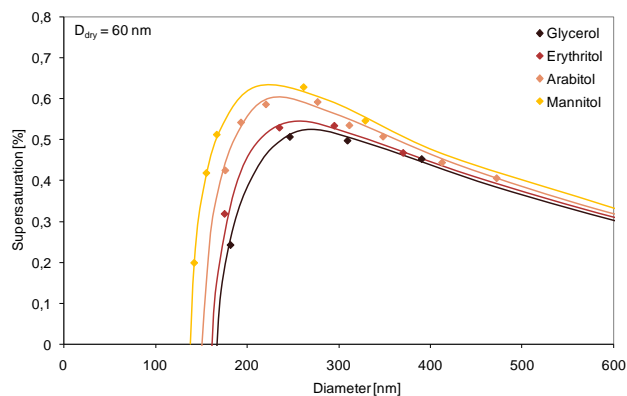


Fig. 2. Köhler curves obtained for polyol solutions. Diamonds Polyols (glycerol: black, erythritol: red, arabitol: orange, mannitol: yellow).

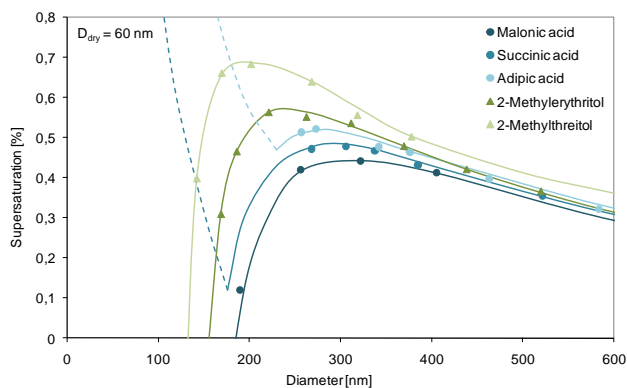


Fig. 3. Köhler curves obtained for 2-methyltetrol and dicarboxylic acid solutions. Triangles: Methyltetrols (2-methylthreitol: light green, 2-methylerythritol: dark green). Circles: dicarboxylic acids (malonic acid: dark blue, succinic acid: medium blue, adipic acid: light blue).

mono- and di-saccharides ($S_c=0.55\text{--}0.85\%$) (Rosenørn et al., 2005). Comparing the Raoult terms in Table 3 shows that the limited CCN efficiencies of polyols and methyltetrols are due to their relatively small Raoult terms and osmolality values. For instance, for $c=0.1\text{ M}$ the expressions in Table 3 give: $C_{\text{osmol}}=210\times 10^{-3}\text{ kg}^{-1}$ for $(\text{NH}_4)_2\text{SO}_4$, $=174\times 10^{-3}\text{ kg}^{-1}$ for NaCl, $=110\text{ to }117\times 10^{-3}\text{ kg}^{-1}$ for the organic acids, $=97\text{ to }112\times 10^{-3}\text{ kg}^{-1}$ for the linear polyols, and $=51\text{ and }42\times 10^{-3}\text{ kg}^{-1}$ for methylerythritol and methylthreitol, respectively, (all with uncertainties of $\pm 14\times 10^{-3}\text{ kg}^{-1}$). The different osmolality values between different classes of compounds in Table 3 generally correlate with the degree of dissociation of these compounds: polyols would not dissociate much, producing only one molecule of solute, organic acids partly dissociate, producing between 1 and 2 molecules of solute, and the inorganic

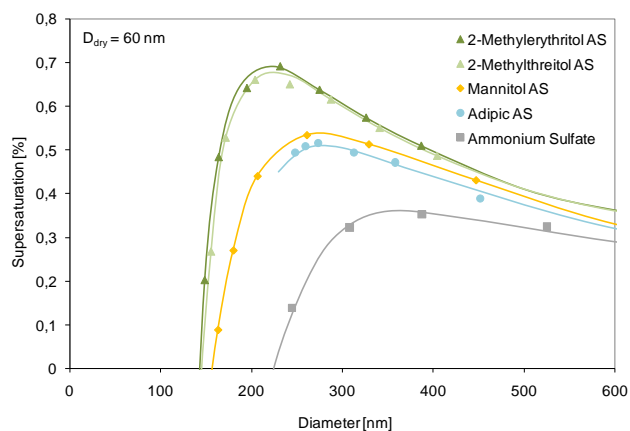


Fig. 4. Köhler curves for mixtures of organic compounds and ammonium sulphate (17% wt/wt). Purple squares: pure ammonium sulfate. Other compounds as in previous Figures.

Table 4. Comparison of the critical supersaturations for dicarboxylic acids determined with the method presented in this work with results from on-line measurements and theoretical values (dry diameter=100 nm).

Compound	This study	Previous studies	Theoretical value
Malonic acid	0.20	0.24 ^a , 0.23 ^b , 0.17 ^{c*}	0.23
Succinic acid	0.22	0.21 ^a , 0.27 ^b , 0.4 ^{d*}	0.25
Adipic acid	0.25	1.0 ^a , 1.65 ^b , 0.4 ^{d*} , 0.62 ^e	0.30

* Values are obtained by extrapolation of experimental data.

^a Prenni et al. (2001)

^b Hori et al. (2003)

^c Giebl et al. (2002)

^d Corrigan and Novakov (1999)

^e Cruz and Pandis (1997)

salts completely dissociate, producing 2 (NaCl) or more ((NH₄)₂SO₄) molecules of solute. This was expected because of the equivalence between C_{osmol} in Eq. (2) and the term containing the Van't Hoff factors in the simplified Köhler equation. However, as mentioned above and in Kiss and Hansson (2004), osmolality also takes into account electrostatic interactions between the molecules of solute that the Van't Hoff factors do not. These smaller effects can be seen in the different osmolality values obtained with different polyols and acids.

For some organic compounds, such as organic acids, surface tension effects can partly compensate for small Raoult effects and improve the CCN efficiency (Facchini et al., 1999). The surface tensions measured in this work as function of the molar concentration, c (M), are summarized in Table 3. For $c=0.1$ M, the surface tension for solutions of adipic and succinic acid were $\sigma_{\text{sol}}(0.1 \text{ M})=66$ and

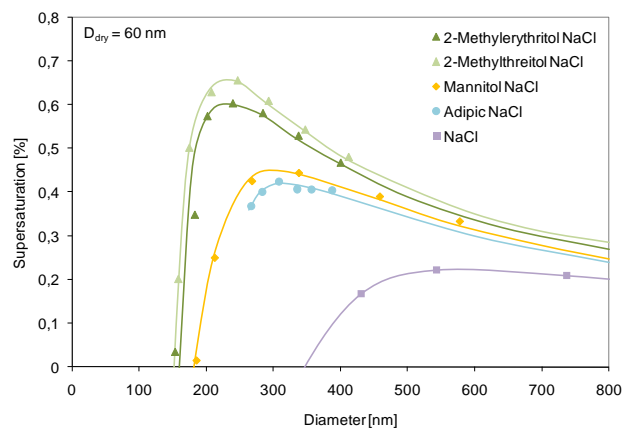


Fig. 5. Köhler curves for mixtures of organic compounds and sodium chloride (17% wt/wt). Grey squares: pure sodium chloride. Other compounds as in previous Figures.

70 (± 1) mN m⁻¹, respectively. None of the linear polyols displayed any significant surface tension effect ($\sigma_{\text{sol}}(0.1 \text{ M}) \sim 71 \pm 1 \text{ mN m}^{-1}$), but the 2-methyltetrols displayed a small effect: $\sigma_{\text{sol}}(0.1 \text{ M}) \sim 70 \text{ mN m}^{-1}$ for both of them. These effects contributed to lower their critical supersaturation, but not enough to be better CCN material than inorganic salts or even organic acids.

3.2 Organic/salt/water mixtures

The measurements of C_{osmol} and σ_{sol} for the organic/salt/water mixtures are also presented in Table 3 and the Köhler curves in Figs. 4 and 5 (all for a dry diameter of 60 nm and a salt composition of 17% wt/wt). For adipic acid with sodium chloride, our results are in agreement with those of Bilde and Svenningsson (2004) showing a strong reduction the critical supersaturation compared to the water mixtures ($S_c=0.52\%$ in water and 0.42% in NaCl, $\pm 0.02\%$), and a slight increase in the critical diameter. This agreement shows that our experimental method remains valid when applied to organic/salt mixtures.

Ammonium sulfate was found to have less impact on the critical supersaturation than sodium chloride ($S_c=0.51\%$). This probably results from the different pH of these salts: sodium chloride solutions are slightly basic (pH=7–8), favoring the dissociation of weak acids, while ammonium sulfate solutions are slightly acidic (pH=5.5–7) and limit their dissociation.

For mannitol, the critical supersaturation was reduced by both salts: from $S_c=0.62\%$ in water, to 0.45% in NaCl, and 0.54% in (NH₄)₂SO₄. This suggests that mannitol is only partly soluble in water, in agreement with the moderate solubility reported in Table 1. As with adipic acid, the critical supersaturation was less reduced by ammonium sulfate than by sodium chloride. By contrast, the critical supersaturation of methylthreitol was hardly affected by the presence

of either salt: $S_c=0.69\%$ in water, and 0.66% NaCl, and 0.68% in $(\text{NH}_4)_2\text{SO}_4$. This lack of effect of salt suggests a very large solubility of this compound in water, in line with the solubility of threitol (Table 1). Interestingly, the critical supersaturation for methylerythritol was increased by both salts: $S_c=0.58\%$ in water, 0.60% in NaCl, and 0.69% in $(\text{NH}_4)_2\text{SO}_4$. A possible explanation for this surprising result is that this compound, as erythritol (Table 1), is only partly soluble in water. However, unlike the di-acids and polyols, the non-soluble part would be liquid not solid, and might form a film at the surface of the droplets, which would limit the uptake of water and therefore the CCN efficiency.

4 Conclusion and atmospheric implications

In this work, complete Köhler curves for a series of C3-C6 polyols and methyltetrols were determined from experimental measurements of the osmolality and surface tension of their organic/water and organic/salt/water solutions. The excellent agreement between the critical supersaturations obtained with this method for malonic, succinic, and adipic acid with on-line techniques and theoretical values demonstrates the validity of this method. The Köhler curves for the C3-C6 polyols and 2-methyltetrols showed their lower CCN efficiency than organic acids, both in water and in the presence of salts. These results indicate that high water solubility does not necessarily imply high CCN efficiency. They are also in line with the low CCN efficiencies determined previously for saccharides. Thus, saccharides and polyols would not contribute more to cloud formation than other organic compounds studied so far. In particular, the presence of 2-methyltetrols in aerosols, believed to result from the oxidation of isoprene, would not enhance cloud formation in the atmosphere, in contrary to recently suggested (e.g. Silva Santos et al., 2006; Meskhidze and Nenes, 2006).

However, under certain conditions, it is possible that highly soluble organic material might activate smaller CCN. In pristine environments such as remote marine regions and the Amazonian wet season, where CCN numbers are limited, this might somewhat increase these numbers and, in turn, affect droplet size. The importance of such effect remains however to be determined.

Acknowledgements. Erik Swietlicki, Lund University, Sweden, and Greg Roberts, CNRM, France, are gratefully acknowledged for their useful discussions. Ulla Widequist, Stockholm University, is thanked for her help with the instruments. B. N. acknowledges support from the European Commission, Marie Curie Chair EXC2005-025026, and International Reintegration Grant IRG2006-036547, and from the Swedish Research Council (research grant NT-2006-5066).

Edited by: T. Hoffmann

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