The role of NH_3 and amines in atmospheric H_2SO_4/H_2O nucleation

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In the lower troposphere, new particle formation is strongly connected to the occurrence of H_2SO_4 with concentrations of about 10^5 - 10^7 molecule cm^{-3} and the nucleation rate of new particles can be described by a power law equation for H_2SO_4 with an exponent in the range of 1 - 2 (Riipinen et al., 2007). Recently, as a result of laboratory studies, nucleation was observed for nearly atmospheric concentrations of H_2SO_4 and also the dependence of nucleation rate on H_2SO_4 concentration was adequately reproduced (Sipilä et al., 2010). NH_3 is believed to represent a third body in the atmospheric nucleation process and theoretical studies proposed that atmospheric mixing ratios of NH_3 at pptv-level can stabilize the critical cluster (Coffman and Hegg, 1995). As a result of quantum chemical calculations, Kurten et al. (2008) concluded that amines can more efficiently support the nucleation process than NH_3.

In the present study, the nucleation enhancing effect of NH_3 and a series of selected amines has been studied experimentally in the atmospheric flow tube *IfT*-LFT (Berndt et al., 2005). Addition of $1.2 \cdot 10^{11}$ or $1.2 \cdot 10^{12}$ molecule cm^{-3} of NH_3 (NH_3 background < $2.5 \cdot 10^9$ molecule cm^{-3}) revealed that NH_3 has a promoting effect on both nucleation rate and particle growth, cf. Fig.1. The enhancing effect was found to be more pronounced under relatively dry conditions. Explaining this behaviour, it can be speculated that there is probably a competition of H_2O vapour (or any H_2O clusters) and NH_3 in the process of critical cluster stabilization. Note, NH_3 levels of $1.2 \cdot 10^{11}$ or $1.2 \cdot 10^{12}$ molecule cm^{-3} stand for atmospheric peak concentrations. Beside the NH_3 data, in Fig.1 the nucleation enhancing effect by tert-butylamine is demonstrated for relatively high amine concentrations being representative for areas with intensive stock farming. Additions of $1.5 \cdot 10^{11}$ or $7.5 \cdot 10^{11}$ molecule cm^{-3} of tert-butylamine show a much stronger effect on nucleation and growth than the comparable NH_3 addition. This behaviour is qualitatively in line with the predictions given by Kurten et al. (2008).

From these measurements it can be concluded that in the "base-polluted" atmosphere (mainly in areas with intensive agricultural activities) the nucleation rate can be significantly higher than for the "clean" atmospheric case (relatively low NH_3 and amine concentrations).

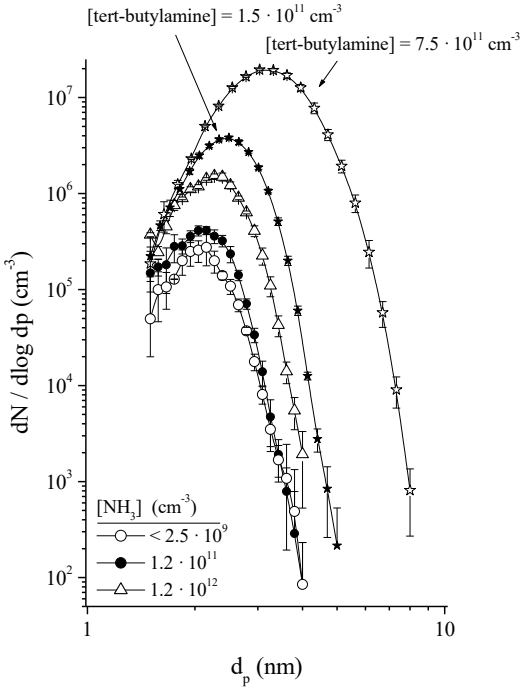

Fig.1. Size distributions for different NH_3 and amine additions, RH:47%; $[H_2SO_4] = 2 \cdot 10^8$ molecule cm^{-3}.

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