

***ADSORPTION OF ORGANIC MOLECULES MAY EXPLAIN GROWTH OF  
NEWLY NUCLEATED CLUSTERS AND NEW PARTICLE FORMATION***

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Extended Abstract

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# Adsorption of Organic Molecules May Explain Growth of Newly Nucleated Clusters and New Particle Formation

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**Abstract.** New particle formation consists of formation of thermodynamically stable clusters from trace gas molecules (homogeneous nucleation) followed by growth of these clusters to a detectable size. Because of the large coagulation rate of clusters smaller than 3 nm with the pre-existing aerosol population, for new particle formation to take place, these clusters need to grow sufficiently fast to escape removal by coagulation. Previous studies have indicated that condensation of low-volatility organic vapor may play an important role in the initial growth of the clusters. However, due to the relatively high vapor pressure and partial molar volume of even highly oxidized organic compounds, the strong Kelvin effect may prevent typical ambient organics from condensing on these small clusters. Earlier studies did not consider that adsorption of organic molecules on the cluster surface, due to the intermolecular forces between the organic molecule and cluster, may occur and substantially alter the growth process under sub-saturated conditions. Using the Brunauer-Emmett-Teller (BET) isotherm, we show that the adsorption of organic molecules onto the surface of clusters may significantly reduce the saturation ratio required for condensation of organics to occur, and therefore may provide a physico-chemical explanation for the enhanced initial growth by condensation of organics despite the strong Kelvin effect.

**Keywords:** Adsorption, New particle formation, Kelvin effect.

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## INTRODUCTION

Atmospheric aerosols strongly influence climate by changing the reflectivity and lifetime of clouds<sup>1, 2</sup>. Model simulations show that nearly half of the global cloud condensation nuclei in the atmospheric boundary layer may be formed through new particle formation<sup>3</sup>. New particle formation is a two-stage process consisting of homogeneous nucleation of thermodynamically stable clusters followed by growth of these clusters to a detectable size (i.e., diameter greater than 3 nm)<sup>4</sup>. Due to the large coagulation rate of clusters smaller than 3 nm with the pre-existing aerosol population, for new particle formation to take place, these clusters need to grow sufficiently fast to escape removal by coagulation<sup>5</sup>. While some previous modeling and field studies indicated that condensation of low-volatility organic vapors may play an important role in the initial growth of the clusters<sup>6, 7</sup>, it is also suggested that due to the high vapor pressure and partial molar volume of even highly oxidized organic compounds,

the strong Kelvin effect at small particle size may prevent typical ambient organics from condensing on these clusters<sup>8, 9</sup>. However, earlier studies did not consider that adsorption of organic molecules on the cluster surface, due to the intermolecular forces between the organic molecule and cluster, may occur and substantially alter the growth process under sub-saturated conditions. Here we examine the effect of adsorption on equilibrium saturation ratio over particle surface and the initial growth of the particles.

## METHODS

The multilayer adsorption of organic molecules onto a flat surface can be described by Brunauer-Emmett-Teller (BET) isotherm<sup>10</sup>:

$$\theta = \left( \frac{1}{1-x} \right) \left( \frac{cx}{1-x+cx} \right) \quad (1)$$

where  $\theta$  is the fractional coverage of the surface by the adsorbed molecules, in layers.  $x$  is the activity of the adsorbing molecule in the gas phase, and can be expressed as its partial vapor pressure  $P$  divided by its saturation vapor pressure over a flat surface,  $P_L^\circ$  (i.e., vapor pressure of the organics in pure liquid or subcooled liquid state). The parameter  $c$  is given by:

$$c = \exp\left(\frac{-\Delta G}{RT}\right) = \exp\left[\frac{-(\Delta G_{ads} - \Delta G_{liq})}{RT}\right] \quad (2)$$

where  $R$  is the gas constant,  $T$  is the temperature,  $\Delta G_{ads}$  is the adsorption free energy of organic molecules on the sites at the particle surface (i.e., 1<sup>st</sup> layer), and  $\Delta G_{liq}$  is the adsorption free energy of organic molecules onto the multilayer (i.e., liquefaction). Equation (1) can be solved for  $x$  to obtain:

$$x = \frac{P}{P_L^\circ} = \frac{[c - \theta(c-2)] - \sqrt{c^2(\theta-1)^2 + 4\theta c}}{2\theta(1-c)} \quad (3)$$

For a growing particle, we also need to consider the Kelvin effect, which increases equilibrium vapor pressure over the particle surface. As a result, the equilibrium saturation ratio over the growing cluster/particle with diameter of  $D$  becomes:

$$S = \frac{P(D)}{P_L^\circ} = \frac{[c - \theta(c-2)] - \sqrt{c^2(\theta-1)^2 + 4\theta c}}{2\theta(1-c)} \cdot \exp\left(\frac{4v\sigma}{RTD}\right) \quad (4)$$

where  $\sigma$  is surface tension, and  $v$  is the molar volume of adsorbed organics. The coverage  $\theta$  can be derived using the following approach. The number of organic

molecules adsorbed to the cluster can be related to the initial cluster diameter  $D_{init}$  and the diameter after sorption,  $D$ , by:

$$N = \frac{\frac{\pi}{6}D^3 - \frac{\pi}{6}D_{init}^3}{\frac{\pi}{6}d_o^3} = \frac{D^3 - D_{init}^3}{d_o^3} \quad (5)$$

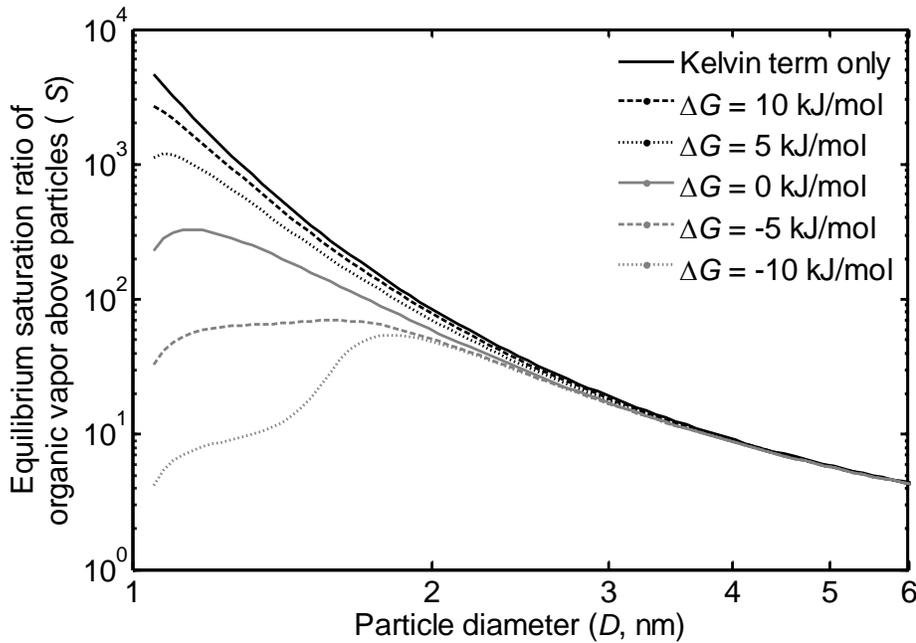
Where  $d_o$  is the diameter of organic molecule. The coverage is then given by:

$$\theta = N \frac{\frac{\pi}{4}d_o^2}{\pi D_{init}^2} = \frac{D^3 - D_{init}^3}{d_o^3} \frac{d_o^2}{4D_{init}^2} \quad (6)$$

Combining Eqn (4) and (6), we can then derive  $S$ , the equilibrium saturation ratio above particle surface, as a function of particle diameter  $D$ .

## RESULTS

The value of  $\Delta G$  is estimated from the data on the adsorption of organics on sulfate particles published in earlier studies<sup>11</sup>. The result suggests that  $\Delta G$  is typically on the order of a few kJ/mole, and may be negative for the adsorption of organic compounds on inorganic salts. The equilibrium saturation ratio  $S$  over a growing particle with an initial diameter  $D_{init}$  of 1 nm is calculated as a function of  $D$  for  $\Delta G$  ranging from -10 to 10 kJ/mole, and the results are shown in Fig 1. In the calculations, the surface tension and molar volume of the organics are assumed as 0.04 N/m and 135 cm<sup>3</sup>/mole, respectively.



**FIGURE 1.** Equilibrium saturation ratio above growing particles when only Kelvin effect is taken into consideration (blue solid line) and those when the effect of adsorption is included. The effect of adsorption was calculated assuming values of  $\Delta G$  ranging from -10 to 10 kJ/mole.

Figure 1 shows that adsorption may significantly reduce the equilibrium saturation ratio over particle surface. This impact depends on the value of  $\Delta G$ . At  $\Delta G = -10$  kJ/mole, including the effect of adsorption reduces the minimum saturation ratio required to grow particles by a factor of  $\sim 100$  (i.e., from 5000 to 50). Even at  $\Delta G = 0$ , the minimum saturation ratio is lowered by about a factor of 10.

## CONCLUSIONS

We show adsorption of organic molecules on the surface of nucleated clusters may significantly reduce the saturation ratio required to grow the clusters by a factor up to 100. This may offer one possible mechanism that allows ambient organics to contribute to the growth of freshly formed clusters despite the strong Kelvin effect.

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