

## ***Interactive comment on* “The effect of H<sub>2</sub>O adsorption on cloud-drop activation of insoluble particles: a theoretical framework” by R. Sorjamaa and A. Laaksonen**

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We would like to thank both referees for their comments.

Referee #1: "The authors selected two isotherm models for assessment. However, other models exist. Is there a physical basis for the selection of the BET and FHH isotherms? Should others be tested?"

Referee #2: "The authors proposed that the theory may work for organic, completely wettable, insoluble compounds; no attempts however were made to address issues on activation of insoluble particles to which a substantial part of the introduction was devoted. Two models of adsorption were tested, however the connection between the physical basis of these models (and specifically the assumptions behind them) to the

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activation process is not discussed. Therefore, the selection of the two models seems somehow arbitrary."

Answer: Model selection in this paper is based above all on practical issues, that is, the amount of data available. There is plenty of adsorption data available for lower saturation ratios and compounds that are not completely wettable but less for high saturation ratios and even less for completely wettable surfaces. Two very popular adsorption models (BET and FHH) were chosen as there was data available to limit the parameter range.

Referee #2: "The most important issue is that of timescales. It is important to clarify that it is thermodynamic equilibrium to what Köhler theory refers to, rather than droplet growth. Thus the authors technically are not describing droplet growth but rather a three-phase equilibrium which they propose to be driven by the physical adsorption of water vapor on a solid surface. This is a significant distinction as it leaves the kinetic contribution to the growth of droplets unresolved. Considering this, a question can be raised on why the authors didn't explicitly address the results of Mahata and Alofs (1974, as cited in the paper) where they reject the idea of water vapor adsorption to be important at atmospheric conditions on the basis that it is a very slow process? In other words, what is the time scale of the water vapor adsorption process, and is it relevant for droplet formation?"

Answer: Just like referee #2 points out, we have not considered droplet growth kinetics as the study is based on Köhler theory, which is an equilibrium theory. We will point this out more clearly in the revised manuscript. Mahata and Alofs (1974) found that droplets form on a macroscopic flat surface with a nonzero contact angle at a supersaturation which is more or less in agreement with the classical heterogeneous nucleation theory, and that at 25% lower supersaturation droplets do not form even after hours of waiting. Their interpretation was that "if adsorption of water tends to negate the [classical] theory, the process is a slow one". So, they in fact did not make any conclusions regarding the timescale of adsorption per se (and it would have been impossible for them as they

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monitored droplet formation, not adsorption). One can make a rough estimation that adsorption rate equals the rate of molecular collisions times sticking probability. If the sticking probability is unity, one monolayer is adsorbed in about  $10^{-6}$  seconds at a vapor pressure of one torr. If monolayer adsorption takes hours, it indicates the sticking probability to be around  $10^{-10}$ , which seems like a fairly low number, especially for completely wettable surfaces.

Referee #2: "The study shows the FHH model to work better than the BET model at describing the onset of activation. This can be expected as there is an extra parameter in the FHH theory that allows more flexibility in reproducing experimental data. However the physical reasons for this are not clear, i.e. why an extra parameter is needed? Is there anything incompatible in the assumptions of the BET model that would preclude its application in this case? This goes back to the fundamental question of what is the meaning of the parameters A, B, and c and how are they related to the properties of the insoluble CCN."

Answer: All adsorption models are more or less approximations of the reality. BET model assumes adsorption heat to be constant, i.e. independent of the thickness of the adsorption layer. This is a good assumption when several layers of water molecules have adsorbed on the surface and the adsorption heat is equal to the condensation heat of water. The parameter in BET-isotherm is related to the heat of adsorption. FHH isotherm is closer to reality as the adsorption layer is expected to become liquidlike only after three or four monolayers. The FHH model can be derived by considering a liquid-like adsorbate on a free adsorbent surface, and the (intermolecular) potential field in which an adsorbate molecule is moving. The parameter A characterizes interactions between adsorbed molecules and between the surface and adjacent adsorbate molecules (i.e. those in the first monolayer). B characterizes the attraction between the solid surface and the adsorbate in subsequent layers. The smaller the value of B, the greater the distance at which the attractive forces act. The values of A and B can be calculated for simplified model potentials (e.g. Van der Waals), but in practice, with real

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adsorbates and adsorbents, they must be treated as adjustable parameters, and the ranges of their values can only be deduced from experimental data.

Referee #2: "The authors conclude that the water activity (solute) term can be described by "any" multilayer adsorption model however they show BET not to be appropriate. What would be the requirements of an adsorption model to work well in this case?"

Answer: Our study shows that FHH model is more flexible than BET when the saturation ratio is high, but this does not prove that BET model is all wrong. It might be that adsorption occurs in a very similar manner for all wettable compounds when relative humidity is close to 100%. As far as we know, there is no experimental data to confirm or deny this. We will clarify this in the revised manuscript.

We will make the technical corrections suggested by the referees to the revised manuscript.

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