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Interactive comment on "Heterogeneous uptake of amines onto kaolinite in the temperature range of 232–300 K" *by* Y. Liu et al.

Anonymous Referee #1

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The authors report uptake coefficients of three amines (methylamine MA, dimethylamine DMA, trimethylamine TMA) on a mineral dust model substance (clay mineral kaolinite) using a Knudsen reactor in the temperature range 232-300 K. Using a simple thermodynamic model for non-reactive systems (P. Davidovits) they go on to interpret the negative T-dependence in terms of adsorption enthalpies and entropies. The paper reads well, however, the authors do not direct their attention to conveying a take-home lesson from their experiments because there are too many loose ends that are not explained or interpreted correctly. Almost all experiments leave wanting to such an extent that the level and quality of effort is not commensurate with the expectations of the readers of acp. The problem is that both kinetics and spectroscopy parts are "light", thus incomplete and misleading. Some of the conclusions are not supported by experimental fact and are left hanging. An example is the assertion that the amines interact with Lewis acid sites on the kaolinite despite the fact that the authors insist on identifying protonated amines in the DRIFTS spectra which would correspond to Bronsted acidic sites on kaolinite, unless I misunderstand. However, only DMA shows protonated base (Figure 2), no evidence is presented for TMA and MA. This is just an example for the severe flaws and shortcomings of this report that prevents the reader from understanding the initial question posed and its eventual resolution. I conclude that his paper is nowhere near to being publishable and I therefore list the most important questions and concerns for the benefit of the authors that need to be answered to the satisfaction of the editor before publication may be envisaged.

I would like to begin with several technical questions that need to be answered such that the interested reader may see for himself rather than taking the author's word for it: trust is good, control is better!

- I have not found a diagram of the Knudsen reactor in any of the author's papers. I assume, that their machine does not include molecular beam modulation and recovery of the chopped signal using a lock-in amplifier. This is usually a fatal flaw in case one is dealing with "sticky" compounds like the present amines. I strongly suggest that the authors include a block diagram (as an Appendix) on the design of the instrument.

- The authors do not seem to ever perform (or report the results of) reference (blank) experiments with the empty sample compartment exposed to the amines. Owing to the day-long (8 h) saturation of the internal vessel walls with the amines one cannot be sure about the interpretation of the signal lasting just 10 to 20 minutes during which "saturation" of the substrate takes place. This is definitely the wrong instrument to tackle the problem at hand.

- I am missing a Table with all salient parameters of the Knudsen reactor such as gas-wall collision frequency, volume and surface of the flow reactor, sample surface, used escape rate constant, flow rate calibrations, MS sensitivities, etc.

- Regarding the low-temperature runs I am missing a detailed sketch (again in the Appendix) of the cooling module: are the feeding lines for the coolant insulated inside the Knudsen reactor? Are the authors sure that the amines are not exposed to additional cold surfaces in low temperature runs? Again, let the reader see ALL the DETAILS! Let the reader make the decision as to the validity of the chosen experimental set-up. Most importantly, I have not seen any blanks with the empty cold cell at the lowest temperatures used. This is a must in order to instill a minimum of confidence in your experiments. In addition, the authors withhold any experimental uptake curves at low temperatures which would be of significant interest to many colleagues!

- Have the authors checked whether or not the uptake corresponds to a first-order rate-law? If the rate law is more complex, and I suspect it is, how good an approximation is a first-order rate law? The Knudsen reactor is a suitable instrument to check out the rate law: one has to vary the rate constant of escape by varying the orifice diameter: if the rate constant for uptake is independent of the orifice diameter, thus the gas residence time, then we have a first-order rate law. Have the authors varied the flow rate? By the way, what was the flow rate of the amine into the flow reactor? One may see that these questions cannot remain unanswered for a halfway complete and reasonable experimental kinetic study on the uptake of amines on kaolinite.

- First and foremost I am missing a calibration of the residual gas MS signals in terms of amine concentrations. To that end I do not understand why the authors use an aqueous solution of the amines. In order to calibrate the amine signals they must use pure amines which are commercially available. One cannot interprete saturation curves such as Figure 1 if one does not have the slightest idea how many molecules of amine it takes to saturate the kaolinite: Does the saturation level correspond to a fraction of a monolayer, one or several layers? These are important questions in order to interpret and grasp the meaning of these saturation experiments.

The following questions are more general:

- Pg. 9, top: What is the typical lifetime of MA, DMA or TMA on the stainless steel

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vessel walls? How does the signal vary with time if you interrupt the flow of amine at once? This should provide the characteristic residence time of the amines on the vessel walls, at least at the beginning because the MS signal decays are complex, unimolecular at the beginning, and more complex at the end.

- Pg. 10, lines 224-226: What is the experimental evidence for the interaction of the amines with Lewis acidic sites on the kaolinite. The same message is recurrent: See also pg. 15, line 359, pg. 16, line 379 and pg. 18, line 412. What is the experimental proof or physical evidence for this? Protonated amines originate from the neutralization of Bronsted, not Lewis acid sites! Furthermore, it is unjustified to postulate protonated MA and TMA from Figure 2. There are no peaks at 1467-1477 cm-1 for these two amines that I can see! To that effect, the authors must amplify and expand the spectrum such that one may distinguish the noise from a potential absorption FTIR signal in the above spectral range.

- How did the authors evaluate the numbers on pg. 11, line 250 (molecules mg-1) in the complete absence of any quantitative calibration of the amine MS signals?

- Regarding Figure 3: The plateau of gamma(obs) seems to be reached for a mass of kaolinite ranging from 20 to 100 mg. Why does the situation change that much for COS/kaolinite (ref. 2010b) in Figure 4 (or reference 2010b) where a sample mass of 20 mg is definitely at the beginning of the linear mass regime (LMR)? In contrast to V. Grassian and coworkers the LMR may be interpreted also in the sense that the mass is not sufficient to cover up the sample surface area with a coherent material layer because there are “holes” in the substrate layer. This depends of course on the particle size. What was the particle size in this study? This information should go into the technical Table requested above.

- On pg. 13 the authors evaluate gamma(eff) using the KML theory. What are the values of the parameters dp, "tau", η, φ, etc. so as to be able to follow the authors in their calculation.

- Pg. 14, line 324 and following: What is the reason the particle size plays such a large role for the magnitude of the uptake coefficient? This question comes up several times without the authors giving an answer.

- It does not make sense to correlate ïĄğgammaeff with pKb of the amines in Figure 4. The latter parameter is dominated by solvent effects because DMA is a stronger base than TMA in solution whereas one expects the inverse. What the authors should take is either the proton affinity (PA or enthalpy of protonation in the gas phase) or gas phase basicity (gB or equilibrium constant). The values are: NH3 (853.6/819.0 kJ/mol corresponding to PA/gB), MA (899.0/864.5), DMA (929.5/896.5), TMA (948.9/918.1). In this series TMA is clearly the strongest base which is an intrinsic property of the molecule compared to MA and DMA.

- Pg. 17, enthalpy and entropy of vaporization: The resulting thermodynamic parameters do not make any sense at all as they are at least a factor of three too small compared to the experimental heat of vaporization of the amines: MA (25.6 kJ/mol), DMA (26.4), TMA (22.94). If the values of the present study were true, then why should the amines interact with kaolinite at all? They certainly will prefer to condense unto itself onto the stainless steel walls into small droplets rather than to adsorb on kaolinite! The reason is that equation (2) is too simple a model for this reactive system. Rather, one must distinguish physisorption from chemisorption. Davidovits did not develop his simple model to a reactive system, therefore, it seems that the simple model is totally inadequate and yields unphysical results.

- Pg. 17, line 404: What did you fit in order to obtain equations (13) to (15)?

- Pg. 19, middle: What is the saturation behavior of the amines at low temperature?

- Pg. 18, line 419-420: “…the uptake of amines was predominantly ascribed to mass accommodation” is hard to understand because mass accommodation is seldom rate-limiting, but transition over a barrier is.

- Table 2, pg. 26: Show raw data at low temperatures!
- Pg. 32, Figure 5: The TMA data lie on a curve, NOT on a straight line! There are important deviations

Some of less important items:

- Pg. 3, line 41: What are “anthropological” emissions?
- Pg. 6, line 138: Tabor et al., 1994, Ullerstam et al., 2003: references are missing.
- Pg. 13, 295: Salgado-Muñoz and„„also in bibliographic list at the end (line 623)!
- Pg. 14, line 327: cluster has the wrong polarity!
- Pg. 14, line 332: Larger than what? The author’s comparison only has one leg!!
- Pg. 15, line 344: What is TEAH sulfate?
- Pg. 20, line 473: mineral dust is a bad reservoir or no reservoir at all! The authors should cut out qualitative or meaningless talk.
- Pg. 23, line 653: “Physiochemical”?
- Pg. 25, Table 1: Under DMA: fifth entry from the top of DMA field has wrong polarity!

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/acp-2016-538/acp-2016-538-RC1-supplement.pdf

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