

Interactive comment on “The effect of varying levels of surfactant on the reactive uptake of N₂O₅ to aqueous aerosol” by V. F. McNeill et al.

V. F. McNeill et al.

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We thank the reviewer for the thoughtful comments, and appreciate their suggestions for how we may clarify our presentation of this work.

Reviewer #1:

My only substantive comment concerns the discussion on page 32. It is not clear at all how the authors determined the surface coverage; one is left to infer that they assumed that surface coverage is a linear function of bulk concentration. For surfactants this is far from true; in fact, if Fig 4b was plotted as “decrease in GAMMA” vs. bulk [SDS], it would strongly resemble the SDS adsorption isotherm. This is exactly how Lawrence et al (2005b) presented the HCl - DCI exchange data cited here. I strongly urge the

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authors to re-analyse their data in this light.

The surface concentration was calculated by assuming that all surfactant present in the aerosol partitions to the surface until the available surface sites are saturated. We agree that a plot of 'decrease in g ' would resemble the SDS adsorption isotherm, it is for this reason that we concluded we have monolayer surface coverage at ~3.5 wt% SDS (i.e. where the decrease in g plateaus). While there was some discussion about this in the manuscript (cf. p. 31 lines 1-22), another statement has been added to make this more explicit. In fig. 4, our primary results (reactive uptake coefficient, g) are plotted as a function of absolute surfactant concentration as well as the derived overall surface concentration. However, we feel that some key information regarding the absolute values of g for NaCl and NSW would be lost, and the overall clarity of presentation would not be greatly improved if we were to present our data in terms of 'decrease in g '. Our interpretation of the Lawrence et al. work that the reviewer references is somewhat different. What appears to be plotted is the fraction of exchange versus butanol bulk concentration. The fact that this fraction increases with butanol loading gives the appearance of an adsorption isotherm. Had it decreased, their figure would appear as our Figure 4.

Other comments: Figures 2 and 4 are formatted too small; it is difficult to make out the different symbols.

The change has been made.

Page 19: Mmerekı et al {J Phys Chem A 107, 11038-11042 (2003) and Atmos Environ 38, 6091-6103 (2004)} reported a strong influence of organic coatings on aqueous surface reactivity.

We regret the oversight, and have added reference to these papers in the introduction.

Page 22, line 13: is 8.8 M NaCl soluble?

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In aerosols such supersaturated solutions are common due to the very small volumes which reduce the probability of forming a germ crystal. NaCl aerosol particles are observed to exist as metastable supersaturated solutions down to 43% RH, well below the deliquescence point of ~75% RH at which the Gibbs free energies for solution and solid are equal. We refer the reviewer to Tang, I. N., Tridico, A. C., and Fung, K. H.: Thermodynamic and optical properties of sea salt aerosols, *J. Geophys. Res.-Atmos.*, 102(D19), 23 269-23 275, 1997.

Page 23, line 18: How was the initial concentration determined? Or was this assumed, based on the vapor pressure?

***The initial concentration was calculated based on the vapor pressure and flow ratios. It is assumed based on previous work (J. H. Hu and J. P. D. Abbatt, *J. Phys. Chem. A*, 1997, 101, 871-878) that this method of N₂O₅ delivery results in a saturated stream of N₂O₅ for slow flows through the cold trap. A statement has been added to make this clear. ***

Page 24, line 16: How was the sensitivity determined?

The sensitivity was determined experimentally by varying the N₂O₅ concentration and observing the change in signal bypassing the aerosol flow tube. We also titrated a flow of NO from a NIST cross-checked cylinder to NO₃+N₂O₅ using O₃ and obtained similar results.

Page 26, line 11: What does “corrected” mean?

The observed rate constants need to be corrected for axial and radial diffusion perturbations to the plug flow assumption (i.e. that injector position is linearly related to reaction time) by using a standard routine developed by Brown (cf. p. 25, line 15). This routine has been employed in numerous flow tube studies of homogeneous and heterogeneous chemistry.

Page 26, line 19: Dotted lines are not shown.

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We thank the reviewer for pointing this out. ‘Grey’ has been substituted for ‘dotted’ in the text.

Page 27, lines 20-25: Are 80% and 87% significantly different in this experiment? (What error estimate is there on these numbers?).

***The yield for N₂O₅ reaction on NaCl aerosol was 87±7%, as stated in the text. It is true that the 80% yield we observe on NSW is within the error of that value, and so the phrase ‘slightly lower than that observed for NaCl’ has been removed. ***

Page 28, line 19: The authors actually observed a lack of suppression of GAMMA, NOT a lack of signs of surfactants on the surface. Is it possible that bromide ions might play some role?

***The wording has been changed to make this distinction, although it should be noted that a suppressed gN₂O₅ value is the only expected sign of organic surfactants at the surface in this study. Yes, it is possible that bromide ions or other inorganic content can explain the enhanced gN₂O₅ in NSW compared with NaCl (cf. p. 28, lines 17-18). But, because we did not observe any Bromine related products, we can not be conclusive in this regard. ***

Page 29, line 19: On what basis do the authors claim “less than 100%”?

***The yield is expected to be less than 100% due to competing bromine reactions. A clarifying phrase has been added. ***

Page 29, lines 24, 25: From where did the Henry’s law and k₆ values come?

***The Henry’s law estimate comes from Fried et al (1994) and Jacob (2000). The references have been added to the text. The “k₆” value was obtained by Thornton et al., 2003 and is technically the product of the rate constant for step 6 in the mechanism and the equilibrium constant for steps 5 forward and reverse: k₆*K_{eq}. The wording has been changed to make this clear, and the description of this calculation has been modified to relate the ratio of the rate constants for step 6 and 7. ***

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Page 31, line 9: Ellison et al did not really add to the extensive literature on surfactant properties; an original reference to the “Pockels limit” would be appropriate here.

***The change has been made. ***

Page 33, line 1,2: Mmereki et al {J Phys Chem A 107, 2264-2269, (2003)} observed changes in ALPHA with sub-monolayer surfactant coverages.

***Mmereki et al. (J Phys Chem A 107, 2264-2269 (2003)) provides important insight on the effects of organic surfactants on gas-liquid interactions. But we feel the anthracene/surfactant/ bulk water system is quite different from the N₂O₅ aqueous aerosol system. In Mmereki et al. (2003), the presence of a sub-monolayer surface coverage of 1-octanol was observed to enhance the physical adsorption of the polycyclic aromatic hydrocarbon anthracene to water. The behavior of surface active organics in the metastable super-saturated ionic solutions of aerosol particles is not nearly as well known. We maintain that we know of no other studies showing a reduction in reactive uptake to submicron aerosol particles due to the presence of surface active organics at sub-monolayer coverages. ***

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 17, 2006.

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