Limitation of water accommodation on organic-coated water surfaces

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Growth of sub-micrometer aerosols is controlled by interfacial mass transfer process which is characterized by mass accommodation coefficient ($0 \leq \alpha \leq 1$). α defined as the probability of a vapor phase molecule entering into the bulk liquid phase after striking the surface (Morita and Garrett, *2008*). The properties of aerosols and droplets containing organic molecules still remain highly uncertain due to the numerous types of compounds that can be present in the atmosphere. Furthermore, mass transfer is more uncertain and poorly established other than any dynamic properties for organic aerosols (Julin *et al* 2014). Our objective is to study the thermodynamic and dynamic of mass accommodation of water on bulk water coated by branched organics with molecular dynamics (MD) simulation in conjunction with umbrella sampling and impinging method in order to explain the limitation of mass transfer of water on organic-coated water surfaces.

The thermodynamic information is gained by studying the free energy profiles of water from gas phase to organic coated bulk water in umbrella sampling simulations. Transition state theory (TST) is used to estimate the α from free energy. TST calculates the equilibrium property and always overestimate the α thus Grote-Hynes theory is used to account the dynamics properties of the surface (Sakaguchi and Morita, *2012*). The simulated organics can be seen on Table 1. These organics are used to examine the dependence of α on carbon density and branched structure.

Table 1. Simulated systems

Case	Molecule	Formula
(a)	water	H_2O
(b)	1-decanol	$C_{10}H_{22}O$
(c)	iso-undecanol	$C_{11}H_{24}O$
(d)	iso-decanol	$C_{10}H_{22}O$
(e)	5,9-dimethyl-1-decanol	$C_{12}H_{26}O$
(f)	3,7-dimethyl-1-octanol	$C_{10}H_{22}O$

The dynamic resistance to water accommodation on organic surfaces is estimated from direct impinging simulations in which a large number of gas molecules striking a liquid surface are virtually explored, and the probability that these molecules will be absorbed into the bulk liquid is statistically derived. We compare the results of α from Grote-Hynes theory and direct impinging simulations, and provide a comparative discussion of their estimates.

To explore a wider range of surface coverage by organic molecules on α, we have performed another set of simulation for a water slab covered with 1-decanol at a lower surface density. Additionally we use three extra estimates at different carbon density from Takahama and Russell (2011) to show the relation of carbon density and α.

We have concluded that carbon density is monotonically related to the mass accommodation coefficient (Figure 1) and can be used to explain the limitation of water accommodation on organic-coated water surfaces.
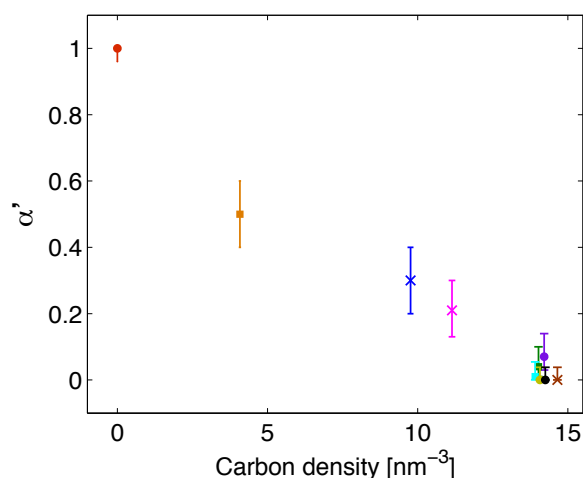

Figure 1. Relationship between α and carbon density. Red, black, yellow, purple, turquoise and green points are for case (a) to (f), respectively. Orange square is for the 1-decanol system at lower surface density. α for pink, blue and brown crossed data are for octanoic, compressed octanoic, and myristic acid systems, respectively and taken from Takahama and Russell (2011).

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