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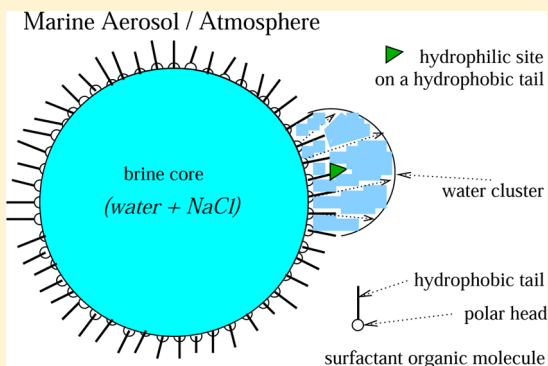
Thermodynamics of Water Condensation on a Primary Marine Aerosol Coated by Surfactant Organic Molecules

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S Supporting Information

ABSTRACT: A large subset of primary marine aerosols can be initially (immediately upon formation) treated using an “inverted micelle” model. We study the thermodynamics of heterogeneous water condensation on such a marine aerosol. Its hydrophobic organic coating can be processed by chemical reactions with atmospheric species; this enables the marine aerosol to serve as a nucleating center for water condensation. The most probable pathway of such “aging” involves atmospheric hydroxyl radicals that abstract hydrogen atoms from organic molecules coating the aerosol (first step), the resulting radicals being quickly oxidized by ubiquitous atmospheric oxygen molecules to produce surface-bound peroxy radicals (second step). Taking these two reactions into account, we derive an expression for the free energy of formation of an aqueous droplet on a marine aerosol. The model is illustrated by numerical calculations. The results suggest that the formation of aqueous droplets on marine aerosols is most likely to occur via Köhler activation rather than via nucleation. The model allows one to determine the threshold parameters necessary for the Köhler activation of such aerosols. Numerical results also corroborate previous suggestions that one can omit some chemical species of aerosols (and other details of their chemical composition) in investigating aerosol effects on climate.



1. INTRODUCTION

Atmospheric aerosols play an important role in the global climate system through their interaction with solar and terrestrial radiation (direct radiative forcing) as well as through their ability to serve as cloud condensation nuclei (CCN) thus affecting the reflectivity of clouds (indirect radiative forcing). The distribution of aerosol and cloud particles with respect to their sizes and chemical composition constitutes a major components of both regional and global climate models.

Heterogeneous condensation is a far more viable way for atmospheric droplets formation than homogeneous condensation. Droplets are formed homogeneously only at rather large vapor supersaturations of water vapor in the atmosphere which are prevented by the presence of foreign nucleating centers.

Among all kinds of nucleating centers, water-soluble ones are believed to be the most efficient CCN. Among soluble nuclei, preexisting liquid aerosols are most widespread in the atmosphere.

Physicochemical properties of atmospheric particles can be affected by heterogeneous chemical reactions of atmospheric species thereupon or/and therein. Since such chemical reactions and the condensation of atmospheric gases/vapors on pre-existing nucleating centers can take place concurrently, it is important to develop an adequate theoretical model for these phenomena that would be simple enough to implement into climate models. So far, heterogeneous condensation has never been studied under conditions of concomitant chemical reactions between vapor-gas medium and foreign particle.

From this standpoint, particularly interesting are aerosols in the marine boundary layer (MBL, the atmosphere between ocean's surface and an altitude of about one to two kilometers), referred to as marine aerosols. Due to the mere extent of MBL (even without considering other relevant factors), marine aerosols constitute an important natural aerosol system. They have been the object of many in situ measurements and experimental studies.^{1–8}

Marine aerosols are conventionally classified into primary and secondary aerosols. Primary marine aerosols are formed by the mechanical, wind produced disruption of the ocean surface. Secondary marine aerosols result from gas-to-particle conversion processes. We will hereafter focus on primary marine aerosols.

Although the size distribution of primary marine aerosols spans a wide range from 10 nm to 10 μm , it is dominated by submicrometre sizes, and in particular, sizes in the range from around 20 nm to around 300 nm.⁶ The dominant mass fraction of marine aerosols is inorganic sea salt, but field measurements provide unquestionable evidence for the presence of organic matter in individual particles¹ and for the contribution of organic species to the fine aerosol mass in the unperturbed marine boundary layer.⁹ Despite a large number of studies on the occurrence of individual compounds or classes of

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compounds, e.g. carboxylic acids,^{10,11} a comprehensive characterization of the chemical nature of organic matter in marine aerosols is currently not available, and the role of organic compounds in the remote marine aerosol, remains largely uncertain, mainly because of the lack of quantitative measurements of their size-dependent composition.

Still, the field measurements^{12,13} have determined that the majority of the organic matter in marine aerosols are water insoluble. Such chemical features of the observed organic matter as the size-dependent concentration, hydrophobic nature of its substantial fraction, low oxidized and surface-active water-soluble organic carbon species therein suggest that bubble-bursting processes at the ocean surface constitute the main source of primary marine aerosols, effectively transferring organic matter into marine aerosol particles, particularly enriching the fine aerosol fraction.^{12,13}

The surface of the ocean is believed to be covered by a monolayer of hydrophobic organics^{4,7} derived from the decomposition of marine organisms that the oceans are teeming with. These hydrophobic molecules (surfactants in water) are thus available for incorporation onto the surface of marine aerosols formed by mechanical ejection from the ocean's surface.

As soon as a primary marine aerosol is formed, water molecules begin to evaporate from the aerosol until a complete hydrocarbon surface monolayer encapsulates it; at that moment the evaporation of H₂O molecules ceases and the aerosol size is stabilized. An initial primary marine aerosol (PMA) is thus coated with organic surfactants (such as, e.g., long-chain hydrocarbons).

In the present work, we consider the condensation of water vapor on a PMA with allowance for concomitant heterogeneous chemical reactions occurring between hydrophobic tails of organic molecules, initially coating PMA, and atmospheric gaseous species. The latter are not directly involved in the nucleation-condensation process but stimulate it by processing the marine aerosol hydrophobic coating and rendering it hydrophilic.

2. INITIAL AND "AGED" MARINE AEROSOLS

Clearly, the exact chemical composition of the aerosol hydrophobic coating (consisting of various organic compounds) depends on where and when (i.e., in which area of the marine boundary layer and in what season of the year) the aerosol was formed; even for aerosols formed in the same area at the same time it can vary from one aerosol to another. Still, most (if not all) of the organic matter at the ocean surface originates from the decomposition of the marine organisms whereof the living cells are enclosed in plasma membranes; their components are all hydrophobic. As cells die and decompose, the hydrophobic cellular constituents accumulate at the ocean surface; phospholipids and fatty acids are common products of lipid membrane disintegration. More than 70% of oceanic fatty acids are in the form of triglycerides, stearyl esters, and phospholipids; phospholipids themselves slowly hydrolyze to fatty acids most of which exist as carboxylates floating at the ocean/atmosphere interface.^{4,14} Consequently, a monolayer of hydrophobic organics, covering the ocean surface, is available for incorporation onto the surface of primary marine aerosols.

For an *initial* primary marine aerosol, it is thus reasonable to adopt a model¹⁵ that considers it to consist of an aqueous (brine) core encapsulated in an inert hydrophobic monolayer (Figure 1). The latter is composed of organic hydrophobic

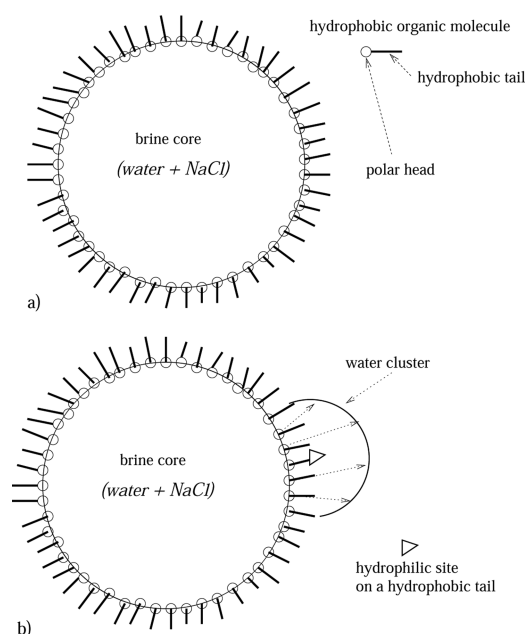


Figure 1. (a) An initial, unprocessed marine aerosol coated by a hydrophobic organic monolayer. (b) The absorption of water molecules by a "processed" marine aerosol. First, water molecules form a globular cluster on the surface of the aerosol around hydrophilic part of radical 2 (shown as an empty circle). Then, unprocessed hydrophobic molecules float up (as shown by dashed arrows) from under the cluster to again find themselves on the surface.

molecules whereof the hydrophilic/polar moieties are attached to the ionic brine core and are pointing inward (to the center of the aerosol) while the hydrophobic (most likely, but not necessarily aliphatic) tails are extending outward to the atmosphere. The organic coating of such an initial PMA is chemically inert and does not react with most atmospheric species (acid, base, H₂O, O₂, O₃, SO₂, NO, NO₂, etc.).

Clearly, there is some probability that the aerosol surface, although composed of hydrophobic moieties, may occasionally (due to fluctuations) *adsorb* some water molecules for a brief period, and there is some probability that some of those (adsorbed) water molecules may be even able to penetrate into the aerosol brine core (again, due to fluctuation). There are no hydrophilic sites on the surface of the initial PMA. Therefore, the probability of the former event (adsorption) can be expected to be very small because the depth of the potential well (assuming Lennard-Jones interactions between a water molecule and all the molecules of the aerosol) is much smaller than the mean energy of thermal (chaotic) fluctuation of the water molecule. For the same reason, even if a water molecule "sticks" to the aerosol surface, its "surface-bound" state will be short-lived, which leads to a low probability of the latter event (penetration); the energetic barrier for the adsorbed water molecule to escape from the aerosol surface into the atmosphere is much lower than the barrier for the same molecule to penetrate into the aerosol core. Thus, one can expect that the surface of an initial PMA will be relatively inert to water molecules and hence such aerosols cannot serve as CCN.

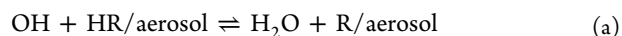
As a natural development of this model (often referred to as an "inverted micelle"), a chemical mechanism was suggested^{4,5} whereby the hydrophobic coating of the aerosol can be "atmospherically" processed ("aged"). The mechanism of

atmospheric aging involves a variety of sequential chemical reactions between organic molecules (coating the aerosol) and atmospheric gaseous species, with atmospheric hydroxyl radicals (and, to a much lesser extent, Cl atoms) playing a crucial role of a "trigger". Incident OH radicals react and create a large number of "free" radical sites on the aerosol organic coating. These radicals are very reactive. The ensuing chain reactions oxidize the marine aerosols so that they become coated with alcohols, aldehydes, alkenes, ketons, carboxylic acid functional groups, etc., so that the hydrophobic coating of the aerosol is gradually transformed into a hydrophilic layer. Consequently, the aged PMA becomes able to serve as a nucleating center for a water droplet. The crucial role of hydroxyl radicals in the heterogeneous oxidation of various submicron organic aerosols in their hydrophobic-to-hydrophilic transformation was demonstrated in several studies;^{16–18} it was reported, for instance,¹⁷ that the OH-initiated oxidative aging of PMAs can drastically increase their hygroscopicity under atmospherically relevant conditions.

Taking into account the foregoing, one can argue that there exists a large subset of marine aerosols whereof the surface is completely covered by a monolayer of various hydrophobic molecules with a general formula HR, where R represents a variety of (mostly hydrocarbon) radicals. In each molecule HR, the radical "R" is essentially the whole molecule less one of the hydrogen atoms, denoted by "H", from the hydrophobic moiety of the molecule; this complementary hydrogen atom H is thus located in the atmosphere. The hydrophilic moiety of the molecule constitutes a part of the radical R and is attached to the brine core.

For example, if the hydrophobic molecule HR is that of hexanoic acid, $\text{CH}_3\text{CH}_2(\text{CH}_2)_3\text{COOH}$, with its polar group $-\text{COOH}$ bound to the brine core and the alkyl tail pointing outward, then the radical R can be either $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{COOH}$, $\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2\text{COOH}$, or $\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_2\text{COOH}$, etc.; the "H" in RH denotes a complementary to R hydrogen atom needed to make a molecule of hexanoic acid. For another example, if the hydrophobic molecule HR is that of palmitoleic acid, $\text{CH}_3\text{CH}_2(\text{CH}_2)_4\text{CH}=\text{CH}(\text{CH}_2)_5\text{COOH}$, with its polar group, $-\text{COOH}$, bound to the brine core and the alkyl tail in the atmosphere, then the radical R can be either $\text{CH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}=\text{CH}(\text{CH}_2)_5\text{COOH}$ or $\text{CH}_3\text{CH}(\text{CH}_2)_4\text{CH}=\text{CH}(\text{CH}_2)_5\text{COOH}$, etc.; the "H" in RH denotes the hydrogen atom needed for R to form a molecule of palmitoleic acid.

The first step of the chemical mechanism, whereby the atmosphere processes the hydrophobic coating of an initial PMA, may consist^{4,5} of hydrogen atom abstraction from the hydrophobic moiety of a surface molecule by an OH radical. Using the above notation, one can write this reaction as

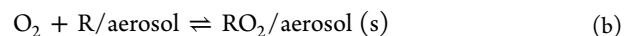


This is an exothermic reaction; in the case where, for example, the hydrophobic molecule RH is that of hexanoic acid, it is accompanied by the release of ~ 20 kcal/mol.

The C–H bond strength depends on whether the hydrogen is primary, secondary, or tertiary; the dissociation energies for these bonds are about 98, 94, and 92 kcal/mol, respectively.¹⁹ In addition, a secondary C–H bond reacts $\sim 40\%$ faster^{20,21} if it is bonded to two $-\text{CH}_2-$ groups rather than to one $-\text{CH}_2-$ and one $-\text{CH}_3$. However, one should keep in mind that the

collisions of OH radicals, impinging onto the aerosols, with the $-\text{CH}_3$ group and the adjacent $-\text{CH}_2-$ group are much more probable than the collisions with $-\text{CH}_2-$ groups situated "deeper" in the alkyl tail; this is due to the particular orientation of carboxylic acid molecules in the aerosol coating. The general formalism developed hereafter is independent of whether it is the abstraction of a primary atom or a secondary one or a tertiary one.

On the second step of the chain reactions processing the hydrophobic coating of the aerosol, the surface-bound radical R produced by reaction a is rapidly oxidized by O_2 molecules, thus producing a new surface-bound radical RO_2



Although the rate constants of reactions a and b are approximately the same,³ the number density of oxygen molecules in the atmosphere is much higher (by more than 12 orders of magnitude) than that of hydroxyl radicals. Therefore, every radical R produced by reaction a is almost immediately oxidized by reaction b.

The further evolution of the surface-bound radical RO_2 , produced by reaction b, may vary but always results in the formation of water-soluble species, volatile species, or hydrophilic radicals, depending on the composition of the atmosphere where the marine aerosol is situated. However, all those transformations mainly involve trace gases and radicals such as NO, NO_2 , O_3 , and HO_2 , which also have much smaller number densities than that of atmospheric oxygen (by 6, in moderately polluted zones, to 10, in remote areas, orders of magnitude).¹⁹ At the same time, the rate constants of their reactions with radicals RO_2 are of the same or smaller order of magnitude than the rate constant of reaction b itself.^{19,4}

Thus, one can conclude that the radicals produced by a reaction of type a in the aerosol surface are immediately oxidized via a reaction of type b by oxygen molecules ubiquitous in the atmosphere. Besides, one can conjecture that chemical transformations following the reaction of type b play a negligible role in the activation of marine aerosols as cloud condensation nuclei. As argued in the next section, the main role in such activation belongs to the sequence of reactions a and b themselves.

3. CONDENSATION ON AND GROWTH OF A MARINE AEROSOL

As outlined above, the aging of the organic aerosol surface by atmospheric radicals creates hydrophilic sites thereupon which can bind water. As a result, water clusters can form owing to the formation of complexes $-\text{O}-(\text{H}_2\text{O})_n$ ($n = 1, 2, \dots$) between water molecules, impinging onto the aerosol, and an oxygen atom present within alkylperoxy radicals or such groups as $-\text{CHO}$, $-\text{CH}_2\text{OH}$, $-\text{COOH}$, etc., in the aged alkyl tails of molecules coating the aerosols. Such oxygen atoms serve as microscopic clusterization centers for the condensation of water molecules on the aerosol. On the basis of high level ab initio calculations,²² the binding energies for various $\text{RO}_2-\text{H}_2\text{O}$ complexes are predicted to range from 2.3 to 5.1 kcal/mol, depending on the composition of the R radical.

Even at relatively very low relative humidity of 10% at 10 °C, the number density of water molecules in the atmosphere is about $3 \times 10^{17} \text{ cm}^{-3}$. This is by 5–9 orders of magnitude greater than the concentrations of such species as NO, NO_2 , O_3 , and HO_2 , which are involved in reactions with RO_2 radicals. Therefore, after a radical RO_2 has been formed, it will be struck

by at least 10^5 water molecules before it collides with any molecule of the above trace species. It is hence reasonable to assume that a water cluster will be formed around the oxygen atom in a radical RO_2 long before this radical undergoes a chemical transformation.

The aging of a marine aerosol of diameter $0.2\ \mu\text{m}$ by the reactions described above (without taking account of cluster formation around the O atom in radical RO_2) would take about $10\ \text{h}$.⁴ On the other hand, if the water vapor supersaturation is not too low (about or higher than 1%), the heterogeneous formation of a water cluster comprising hundreds of molecules would take no longer than several seconds.²³ Thus, during the formation of a water cluster around any radical RO_2 the surrounding surface region is mainly occupied by unprocessed hydrophobic molecules. Therefore, initially, the water cluster around the oxygen atom will have a caplike shape as shown in Figure 1b. However, this cannot last long. Indeed, it is thermodynamically unfavorable for the hydrophobic tails of unprocessed surfactant molecules HR (surrounding the radical RO_2) to be situated between the nascent (water) cluster and brine core; it would have meant that they were stable within the aqueous phase which would not be consistent with their hydrophobic (surfactant) character. Since they are mobile, they will tend to make their way into the newly formed interface “water cluster–air”. Consequently, the water molecules of the cluster will find themselves within the brine core, thus increasing the volume of the marine aerosol and its surface area. Since the total number of surfactant molecules and radicals in the aerosol coating does not change on such short time scales, the corresponding surface coverage decreases. As a result, there appear additional (to radicals RO_2) hydrophilic sites on the aerosol surface (kind of “defects” in its hydrophobic coating) creating a positive feedback to the initial increase of the aerosol size. The condensation of water molecules on to the marine aerosol thus becomes possible.

4. FREE ENERGY OF FORMATION OF AN AQUEOUS DROPLET ON A MARINE AEROSOL

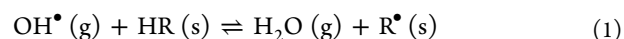
Let us consider a marine aerosol in a mixture of water vapor, hydroxyl radicals, and oxygen, thus neglecting the other components of the atmosphere. In the framework of the above model, it is reasonable to treat the condensation of water vapor on and surface processing of marine aerosols as occurring simultaneously.

The PMA itself is an aqueous particle covered with a monolayer of hydrophobic hydrocarbons. The core of the aerosol is a salt/water “brine” consisting of NaCl and H_2O molecules (dissociation of salt molecules is understood and discussed below). The covering film may consist of fatty acids and/or other organics having a very small solubility; in the case of a fatty acid all its molecules are on the aerosol surface with the polar heads attached to the aqueous core and long hydrophobic tails extending thence to the atmosphere.⁴

The number of water molecules in the aerosol may change due to their condensation from and their evaporation into the atmosphere, but these do not occur as long as the aerosol is coated with hydrophobic molecules. However, the hydrophobic coating itself is gradually processed by reactions with atmospheric OH radicals and O_2 molecules. As a result, the hydrophobic coating of the aerosol is gradually transformed into a hydrophilic layer as discussed in section 2, and there appear more and more sites on the aerosol surface which

atmospheric water molecules can stick to so that heterogeneous condensation of water occurs as discussed in section 3.

Let us rewrite reactions 1 and 2 in the form



explicitly indicating whether reagents and products belong to the gas phase (g) or are surface-bound (s) (none of the components of these reactions belong to the liquid phase (l)), and marking the radical entities with a superscript bullet (\bullet). One can roughly neglect⁴ the processing of initial hydrophobic molecules by Cl atoms or by HO_2 radicals in comparison to the processing by OH radicals.

In what follows, the Greek superscripts α , β , and γ will mark quantities in the internal part of the droplet (α), vapor-gas mixture (β), and internal part of the initial PMA (γ); a double Greek superscript will mark quantities at the corresponding interface. For simplicity, it is assumed that only one kind of salts is present in the aerosol and that the dissociation of its molecules in the initial PMA and droplet is complete. These assumptions hardly affect the generality of the theoretical model, but they significantly simplify the algebra.

Physical quantities for different components of the system will be marked by the following subscripts: “w” for water, “s” for the salt, “0” for initial hydrophobic molecules (coating the initial MA), “1” for radicals RO_2^\bullet produced by reaction 2. The total number of molecules of water, salt, and surfactant molecules in an initial marine aerosol will be denoted as q_w , q_s , and q_0 , respectively. Salt molecules are assumed not to be present in the atmosphere and we neglect their evaporation from the aerosol as well. Thus, the total number of salt molecules (ions) does not change during the evolution of the aerosol into the droplet or afterward (coagulation is not considered in the present work either). The total number of molecules of component i in a droplet, formed on the marine aerosol, will be denoted with ν_i ($i = \text{w}, \text{s}, 0, 1, 2$).

As usual in the thermodynamics of first order phase transitions,^{24–26} the reversible work W of formation of a droplet on a marine aerosol can be determined as the difference $F_{\text{fin}} - F_{\text{in}}$, where F_{in} is the Helmholtz free energy of the initial system (an initial PMA in the vapor-gas mixture of water, hydroxyl radicals, and oxygen), and F_{fin} is the Helmholtz free energy of the system after the formation of the droplet on the PMA (the process of droplet formation is assumed to occur in a canonical ensemble). Expressing the free energy W of formation of a droplet on a marine aerosol in units $k_B T$, with k_B Boltzman’s constant and T the temperature, one can obtain (see the Supporting Information for details)

$$\begin{aligned} W = & -(\nu_w - q_w) \ln(\zeta/\chi_w^f(\chi)) + (\sigma^{\alpha\beta} A^{\alpha\beta} - \sigma^{\gamma\beta} A^{\gamma\beta})/k_B T \\ & + q_w \ln \left(\frac{\nu_w}{\nu_w + q_s} \frac{q_w + q_s}{q_w} \right) - 2q_s \ln \frac{\tilde{m}_s(\chi^\gamma) \tilde{f}_s(\chi^\gamma)}{\tilde{m}_s(\chi) \tilde{f}_s(\chi)} \\ & + q_0 \ln \frac{\pi_0^{\alpha\beta} f_0^{\alpha\beta}}{\pi_0^{\gamma\beta} f_0^{\gamma\beta}} + (\nu_1 + \nu_2) \ln \left(\frac{\pi_1^{\alpha\beta} f_1^{\alpha\beta}}{\pi_0^{\alpha\beta} f_0^{\alpha\beta}} \frac{P_w}{P_{\text{OH}}} \frac{1}{K_1} \right) \\ & + \nu_2 \ln \left(\frac{\pi_2^{\alpha\beta} f_2^{\alpha\beta}}{\pi_1^{\alpha\beta} f_1^{\alpha\beta}} \frac{1}{P_{\text{O}_2}} \frac{1}{K_2} \right) \end{aligned} \quad (3)$$

where P_w , P_{OH} , and P_{O_2} are the partial pressures of water vapor, hydroxy radicals, and oxygen in the atmosphere; $\zeta = P_w/P_{w\infty}$ is the saturation ratio of water vapor, with $P_{w\infty}$ being the equilibrium water vapor pressure; χ' and $\chi \equiv \chi^a$ are the mole fractions of water in the internal part of the initial MA and droplet, respectively; σ and A are the surface tension and surface area of an interface; π_j ($j = 0, 1, 2$) is the partial surface pressure, that is, the decrease in the surface tension of the solvent caused by the adsorption of surfactant j into the interface and f_j is the corresponding surface activity coefficient; in the fifth term on the RHS of the equation, factor 2 is due to the (assumed) complete dissociation of salt molecules in the brine and $m_s(\chi')$ and $\tilde{f}_s(\chi')$ are the mean ionic molality and mean ionic activity coefficient of salt in the solution of composition χ' ; K_1 and K_2 are the equilibrium constants of reactions 1 and 2. Note that the double superscript $\alpha\beta$ for components 1 and 2 are omitted because they can be located in the droplet-atmosphere interface only.

The chemical structures of molecules (radicals) of components 0, 1, and 2 differ relatively little. This allows one to assume that their surface activity coefficients are roughly equal to unity and that, for the partial surface pressures of components 0, 1, and 2, there holds Dalton's law for an ideal mixture of gases. Thus

$$\begin{aligned} f_2^{\alpha\beta} &\simeq f_1^{\alpha\beta} \simeq f_0^{\alpha\beta} \simeq 1, & \pi^{\alpha\beta} &= \pi_2^{\alpha\beta} + \pi_1^{\alpha\beta} + \pi_0^{\alpha\beta}, \\ \pi_j^{\alpha\beta} &= \gamma_j \pi^{\alpha\beta}, & \gamma_j &= \Gamma_j/\Gamma, \\ \Gamma_j &= \nu_j^{\alpha\beta}/A^{\alpha\beta} \quad (j = 0, 1, 2), & \Gamma &= q_0^{\gamma\beta}/A^{\alpha\beta} \end{aligned} \quad (4)$$

The quantity γ_j characterizes the relative surface coverage of the droplet by surfactant species j ; clearly, $\gamma_2 + \gamma_1 + \gamma_0 = 1$.

Furthermore, the similarity of the structure of surfactant species 0, 1, and 2 allows one to assume that the surface tension $\sigma^{\alpha\beta}$ of the real droplet will be roughly the same as it would be if the droplet were coated only with unprocessed molecules of component 4 in quantity q_0 . Thus, the surface tension $\sigma^{\alpha\beta}$ of the droplet can be assumed to be a function of only one variable, $x = q_0/(\nu_w + q_s + q_0)$, so that $\sigma^{\alpha\beta} = \sigma^{\alpha\beta}(x)$. Consequently, the surface pressure will then also be a function of only one variable x : $\pi^{\alpha\beta} = \pi^{\alpha\beta}(x)$. Taking account of eq 4, one can thus reduce eq 3 to

$$\begin{aligned} W &= -(\nu_w - q_w) \ln[\zeta(1 + q_s/\nu_w)] + a(x) \\ &+ (\nu_w m_w + q_s m_s)^{2/3} \omega^{2/3}(\chi_s(\nu_w)) + q_w \ln \frac{\nu_w}{\nu_w + q_s} \\ &+ q_0 \ln \left[\frac{q_0 - \nu_2 - \nu_1 \pi^{\alpha\beta}(x)}{q_0 \tilde{\pi}} \right] - 2q_s \ln \frac{\tilde{m}_s(\chi')}{\tilde{m}_s(\chi)} \\ &+ (\nu_2 + \nu_1) \ln \left(\frac{\nu_1}{q_0 - \nu_2 - \nu_1} \frac{P_w}{P_{OH} K_1} \right) \\ &+ \nu_2 \ln \left(\frac{\nu_2}{\nu_1} \frac{1}{P_{O_2} K_2} \right) + \tilde{W} \end{aligned} \quad (5)$$

where m is the mass of a molecule, $\omega(\chi_s)$ is the specific volume of the aqueous solution of composition $\chi_s \equiv \chi_s(\nu_w) = q_s/(\nu_w + q_s)$, and $a(x) = (36\pi)^{1/3}(\sigma^{\alpha\beta}(x) - \sigma^{\beta\beta}(x_0))/k_B T$, with $x_0 = q_0/(q_w + q_s + q_0)$; the activity coefficients f_w and f_s have been set equal to unity because the core of the droplet (seawater) can be roughly treated as an infinitely dilute solution; $\tilde{\pi} = 0.06084$

dyn/cm; the term \tilde{W} is independent of ν_w, ν_1, ν_2 , but depends on the parameters of the initial aerosol: $\tilde{W} \equiv \tilde{W}(q_w, q_0, q_s) = q_w \ln[(q_w + q_s)/q_w] + q_0 \ln[\pi^{\beta\beta}(x_0)/\tilde{\pi}]$.

As clear from eq 5, W is a function of only three independent variables of state of a droplet: ν_w, ν_1 , and ν_2 . Since W is the free energy of formation of a droplet on a heterogeneous center (marine aerosol), one can expect^{27–31} the function $W = W(\nu_w, \nu_1, \nu_2)$ to determine a free-energy surface (in a four-dimensional space) which has a well point and a saddle point. Hereafter, the quantities for the well and saddle points will be marked with subscripts “e” and “c”, respectively.

Note that equations S13 and S18 (see the Supporting Information) for W are obtained without approximations that would affect the accuracy of the model, whereas eqs 3 and 5 involve approximations of increasing roughness. Their accuracy is subject to the availability of adequate models for the electrolyte and surface chemical potentials, as well as for the surface tension of organically coated droplets.

5. NUMERICAL CALCULATIONS

To illustrate the above presented theory with numerical results, we carried out calculations for various values of the parameters q_w, q_s, q_0, K_1, K_2 , and ζ of the system “initial aerosol + vapor mixture”. Considering various values of the equilibrium constants K_1 and K_2 was necessary to shed some light on the sensitivity of the phenomenon of interest to the chemical composition of the hydrophobic film around the initial PMA.

First, we considered a marine aerosol whereof the core (salt/water brine) is composed of $q_w + q_s \simeq 1.3 \times 10^8$ molecules coated by a monolayer of $q_0 \simeq 6.3 \times 10^5$ surfactant molecules. As was demonstrated (see below), the specific nature of various hydrophobic molecules in the surface film matters only inasmuch as it affects the surface tension of the evolving marine aerosol; we assumed only that they are able to participate in the chemical reactions 1 and 2 with their own equilibrium constants K_1 and K_2 (which is the case of, for example, various phospholipids or carboxylic acids). The composition of the salt/water brine was assumed to be such that $q_w = 1.286 \times 10^8$ and $q_s = 1.4 \times 10^6$ which roughly corresponds to 34 g/kg salinity (recall that the standard mean ocean water (SMOW) salinity is about 35 g/kg). Clearly, if the monolayer, coating the aerosol, is assumed to be complete, with the hydrophobic molecules closely packed on the surface, then the parameter q_0 is not independent because it can be approximately determined through q_w and q_s as

$$q_0 = \frac{1}{a_h} (36\pi)^{1/3} (q_w m_w + q_s m_s)^{2/3} \omega_s^{2/3}(\chi_s(q_w))$$

where a_h is the areal size (i.e., the surface area of a footprint) of a fatty molecule bound to the water surface; in the Pockels limit^{4,32} $a_h \approx 2 \times 10^{-15} \text{ cm}^2$.

The temperature of the system was equal to $T = 293.15 \text{ K}$. The partial pressures of hydroxyl radicals and oxygen were set to be³³ $P_{OH} \simeq 3.7 \times 10^{-8} \text{ dyn/cm}^2$ and $P_{O_2} = 2.06 \times 10^5 \text{ dyn/cm}^2$. For the composition dependence of the surface tensions $\sigma^{\alpha\beta}$ and $\sigma^{\beta\beta}$, we used an analytical fit obtained with Mathematica 8 for the experimental data provided in refs 34 and 35. Since the effect of the droplet surface tension on condensation/nucleation phenomena is well investigated, it was assumed that the surface tension of bulk aqueous solution of hexanoic acid can serve as an acceptable approximation for the surface tension of a marine aerosol, covered by various phospholipids and/or

carboxylic acids and radical groups (resulting from reactions 1 and 2). The curvature effect on $\sigma^{\alpha\beta}$ and $\sigma^{\gamma\beta}$ was neglected.

The equilibrium constants for all surfactant species coating the aerosol were roughly assumed to be $K_1 \simeq 10^{15}$ and $K_2 \simeq 5 \times 10^{-6} \text{ dyn}^{-1} \text{ cm}^2$. The latter corresponds to the several hour lifetime of radical 2 ($\sim 6 \text{ h}$), if the rate constant of the forward reaction 2 is $\sim 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Note that there is some uncertainty concerning the choice of K_2 ; this is due to the absence of any direct data for the rate constant of the reverse reaction in eq 2. Although the value of K_2 has no effect on the ν_w dependence of W at fixed ν_2 and ν_1 and weakly influences the ν_1 dependence of W at fixed ν_w and ν_2 , it does significantly affect the ν_2 dependence of W at fixed ν_w and ν_1 . However, neither K_1 nor K_2 markedly affect the height of the activation barrier that a marine aerosol must overcome to become a nucleating center for an aqueous droplet. The results of numerical evaluations are presented in Figures 2–5.

Figure 2a shows the typical dependence of the free energy $W = W(\nu_w, \nu_2, \nu_1)$, given by eq 5, on the number ν_w of water molecules in the droplet at fixed numbers ν_1 and ν_2 of components 1 and 2 (i.e., radicals R^\bullet and $RO_{2,\bullet}$, respectively), the saturation ratio ζ of the water vapor being $\zeta = 1.0033505$. The variables ν_w , ν_1 , and ν_2 are replaced by the normalized analogs $u_w = \nu_w/q_w$, $u_1 = \nu_1/q_0$, and $u_2 = \nu_2/q_0$, respectively (recall that the free energy W in eq 5 is already expressed in units $k_B T$). The upper curve is for $u_2 = 1.0006u_{2e}$, $u_1 = u_{1e}$, the middle curve is for $u_2 = u_{2e}$, $u_1 = 1.0006u_{1e}$, and the lower curve is for $u_2 = u_{2e}$, $u_1 = u_{1e}$. The variables u_1 and u_2 vary very little from the well point to the saddle one; Mathematica 8 provides $u_{2e} \simeq u_{2c} \approx 0.50723$ and $u_{1e} \simeq u_{1c} \approx 0.49246$. The variable u_w in the well and saddle points is equal to $u_{we} = 14.852$ and $u_{wc} = 15.784$, respectively.

As expected, the free energy as a function of ν_w has a local minimum and a local maximum. Such a dependence is observed for any ν_1 and ν_2 and for any other saturation ratio of the water vapor provided that it is lower than some threshold value (see below). This is a well-known form of the size dependence of free energy of droplet formation in a theory of heterogeneous condensation, both unary^{23,36,37} and multicomponent;^{27–31} it has a minimum at some ν_{we} and a maximum at some $\nu_{wc} > \nu_{we}$, with an inflection point $\tilde{\nu}_w$ between them, $\nu_{we} < \tilde{\nu}_w < \nu_{wc}$ (all in the case where condensation occurs in a fluctuational way). The variable ν_w can thus play the role of an unstable variable of state of a droplet (which is always single in any first order phase transition).

Figure 2b presents the dependence of W on u_2 at fixed $u_w = u_{we}$ and $u_1 = u_{1e}$, whereas Figure 2c shows the u_1 dependence of W at fixed $u_w = u_{we}$ and $u_2 = u_{2e}$. As seen, in both cases the free energy W is concave downward, so that the variables u_2 and u_1 (i.e., ν_1 and ν_2) can be considered as stable variables of state of a droplet (analogous to the composition variables in a theory of multicomponent nucleation, both homogeneous³⁸ and heterogeneous (see, e.g., ref 29 and references therein). One can note that the loci of the minima of W as a function of u_1 (at $u_2 = u_{2e} \simeq u_{2c}$) and the loci of the minima of W as a function of u_2 (at $u_1 = u_{1e} \simeq u_{1c}$) are virtually independent of the unstable variable u_w . Therefore,³² the function $W = W(\nu_w, \nu_1, \nu_2)$ in the vicinity of the well and saddle points can be accurately enough approximated by the quadratic forms

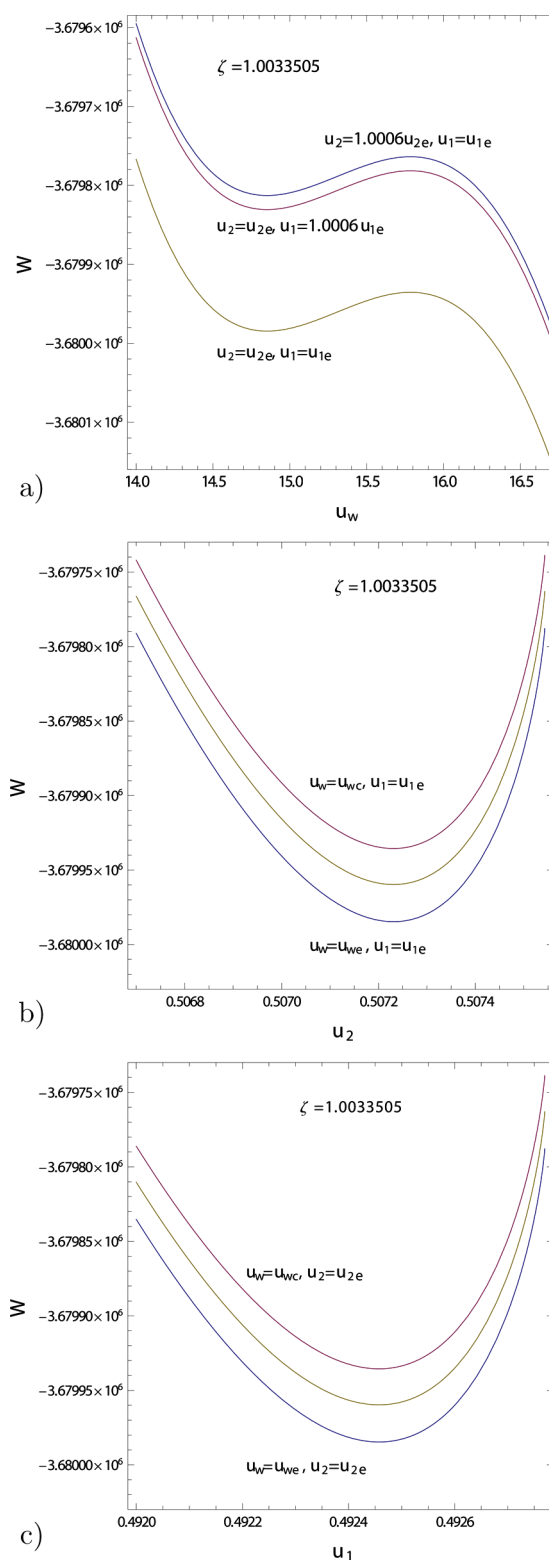


Figure 2. The free energy of formation of a droplet on a marine aerosols as a function of its three independent variables, u_w , u_1 , and u_2 , in the water vapor of saturation ratio $\zeta = 1.00277$, at $T = 293.15 \text{ K}$. The initial marine aerosol consists of $q_w = 1.289 \times 10^8$ water, $q_0 = 6.3 \times 10^5$ surfactant, and $q_s = 1.1 \times 10^6$ salt molecules (corresponding to an aerosol of radius $R = 97.6 \text{ nm}$ and salinity $s = 34.1124 \text{ g/kg}$); a) The free energy W versus the number u_w of water molecules in the droplet at fixed numbers u_1 and u_2 of radicals 2 and 1, respectively; b) The dependence of the free energy W on u_2 at fixed u_w and u_1 ; c) The u_1 -dependence of the free energy W at fixed u_w and u_2 .

$$W = W_e + \frac{1}{2}W''_{ww}(\nu_w - \nu_{we})^2 + \frac{1}{2}W''_{11}(\nu_1 - \nu_{1e})^2 + \frac{1}{2}W''_{22}(\nu_2 - \nu_{2e})^2$$

and

$$W = W_c + \frac{1}{2}W''_{ww}(\nu_w - \nu_{wc})^2 + \frac{1}{2}W''_{11}(\nu_1 - \nu_{1c})^2 + \frac{1}{2}W''_{22}(\nu_2 - \nu_{2c})^2$$

respectively, where W_c and W_e denote the free energies of droplet formation at the saddle and well points, respectively, and W''_{jj} is the second partial derivative of W with respect to ν_j ($j = w, 1, 2$) (at the well and saddle points, as appropriate). This significantly facilitates the development of a kinetic model for the process of overcoming the free energy barrier determined by $W = W(\nu_w, \nu_2, \nu_1)$ if the process occurs via nucleation.

In Figure 3, the unstable character of the variable ν_w and stable character of the variables ν_1, ν_2 are further illustrated with the contour plots of the free energy surface: (a) W versus scaled variables u_w and u_2 at fixed $u_1 = u_{1e}$; (b) W versus scaled variables u_w and u_1 at fixed $u_2 = u_{2e}$; (c) W versus scaled variables u_1 and u_2 at fixed $u_w = u_{we}$. The contours are plotted with a uniform step. Note that the contour lines would change insignificantly if instead of $u_1 = u_{1e}$ (Figure 3a), $u_2 = u_{2e}$ (Figure 3b), and $u_w = u_{we}$ (Figure 3c), they were plotted at $u_1 = u_{1c}$, $u_2 = u_{2c}$, and $u_w = u_{wc}$, respectively.

Unlike homogeneous nucleation whereof the rate is proportional to the exponential of the free energy of formation of a critical nucleus, the rate of heterogeneous nucleation is proportional to $\exp[-\Delta W_{ce}]$, where $\Delta W_{ce} \equiv W_c - W_e$. The quantity ΔW_{ce} determines the height of the free energy barrier to heterogeneous nucleation. In the case of heterogeneous water nucleation on a marine aerosol, $W_c = W(\nu_{wc}, \nu_{1c}, \nu_{2c})$ and $W_e = W(\nu_{we}, \nu_{1e}, \nu_{2e})$.

The height of the free energy barrier depends on the initial size of the aerosol (hereafter characterized by the radius R of the core), its initial salinity s , and the water vapor saturation ratio ζ : $\Delta W_{ce} = \Delta W_{ce}(R, s, \zeta)$. Figure 4 illustrates the sensitivity of ΔW_{ce} to the water vapor saturation ratio and to the marine aerosol initial size and salinity, namely, (a) the dependence of ΔW_{ce} on ζ for a marine aerosol of initial radius $R = 97.6$ nm and initial salinity of $s = 34.1124$ g/kg, (b) the dependence of ΔW_{ce} on the initial radius R of a marine aerosol of initial salinity $s = 34.1124$ g/kg in the water vapor of saturation ratio $\zeta = 1.0033505$, and (c) the dependence of ΔW_{ce} on s for marine aerosols of given size $R = 97.6$ nm at fixed water vapor saturation ratio $\zeta = 1.0033505$. As clear, the height of the nucleation barrier is very sensitive to the initial size and salinity of marine aerosol and is extremely sensitive to the water vapor saturation ratio. The latter result is not unexpected because a similar behavior of the nucleation barrier height has been predicted for heterogeneous nucleation on several kinds of simple nucleating centers.^{23,28,29,36,37}

To clarify the sensitivity of the aerosol activation to the chemical composition of the aerosol hydrophobic coating, we considered an initial PMA of radius $R = 0.0976$ μm and salinity $s = 34.1124$ g/kg in the atmosphere with $\zeta = 1.0033505$ and calculated the height of the activation barrier ΔW_{ce} for various K_1 's ($= 10^{14}, 5 \times 10^{14}, 10^{15}, 5 \times 10^{15}, 10^{16}$) and various K_2 's ($= 5 \times 10^{-7}, 25 \times 10^{-7}, 5 \times 10^{-6}, 25 \times 10^{-6}, 5 \times 10^{-5}$ $\text{dyn}^{-1}\text{cm}^2$).

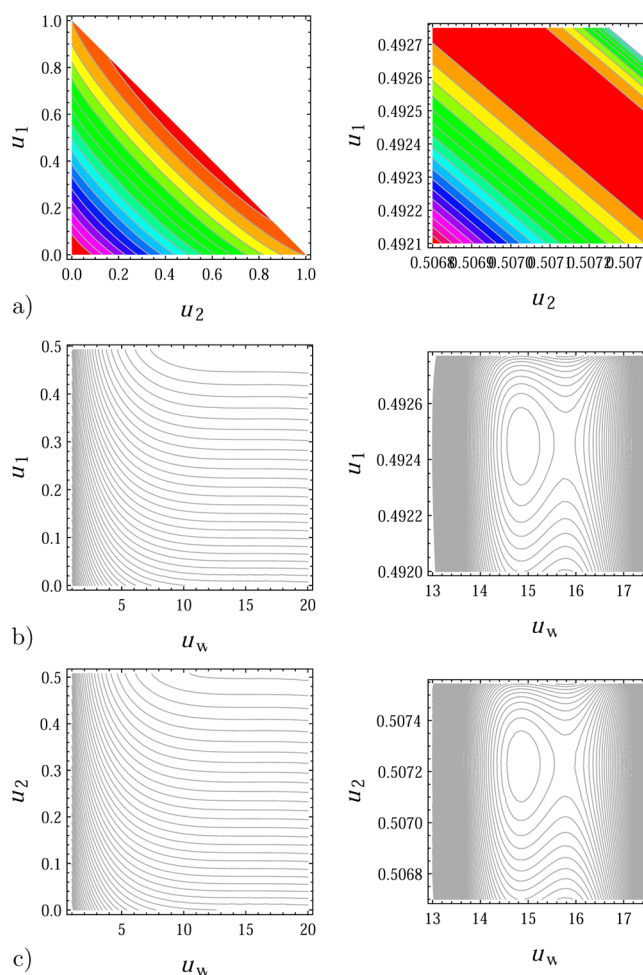


Figure 3. Contour plots of the free energy surface on large and small scales (left and right figure panels, respectively): (a) W vs scaled variables u_1 and u_2 at fixed $u_w = u_{we}$; (b) W vs scaled variables u_w and u_1 at fixed $u_2 = u_{2e}$; (c) W vs scaled variables u_w and u_2 at fixed $u_1 = u_{1e}$. The contours are plotted with a uniform step. In Figure 3a, the warmer colors correspond to lower areas of the free energy surface; the red color stripe (going from top-left to bottom-right) thus corresponds to the lowest area of the free energy surface.

It turns out that the variation of K_1 by 2 orders of magnitude (from 10^{14} to 10^{16}) at any K_2 affects ΔW_{ce} only by about 0.2%. Likewise, the variation of K_2 by 2 orders of magnitude (from 5×10^{-7} to 5×10^{-5} $\text{dyn}^{-1}\text{cm}^2$) at any K_1 leads to a negligible change in ΔW_{ce} (less than 0.4%).

On the other hand, it is well-known that the height of the activation barrier of heterogeneous condensation is very sensitive to the surface tension of droplets. One can thus conclude that the physicochemical processes whereby a marine aerosol, initially encapsulated in a hydrophobic film, is activated and becomes a cloud condensation nucleus, depends on the chemical composition of its hydrophobic coating only through its macroscopic physical property (i.e., the surface tension of the evolving aerosol) rather than on the microscopic chemical characteristics of surfactant molecules and radicals (i.e., the equilibrium constants of reactions 1 and 2). Therefore, the theoretical model proposed above is applicable to a large subset of marine aerosols whereof the hydrophobic coating in the initial state is composed of organic molecules able to participate in the chemical reactions 1 and 2.

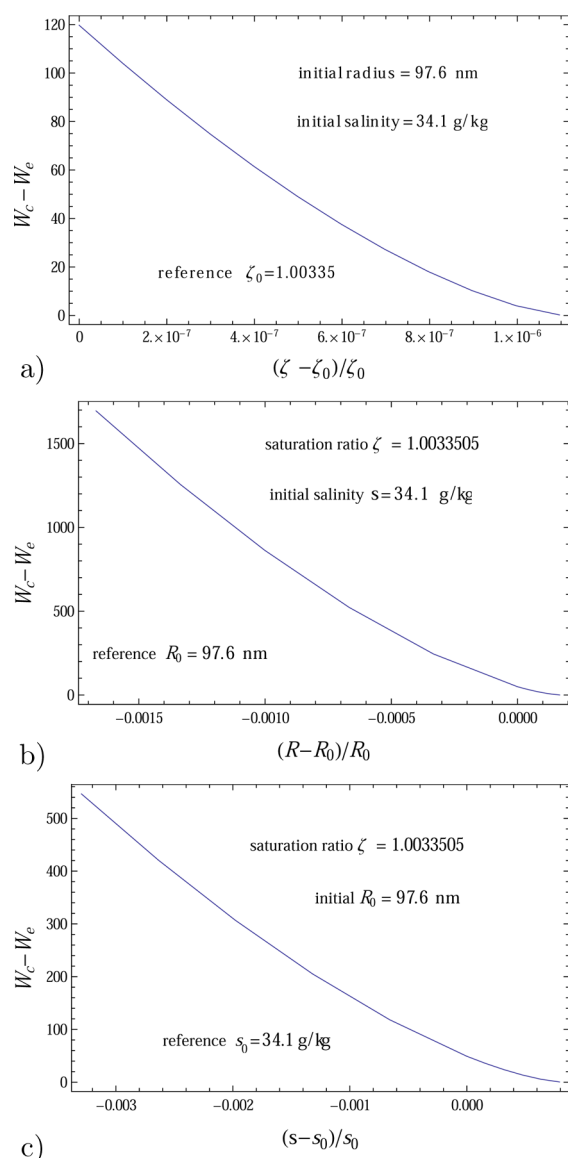


Figure 4. (a) Dependence of the height ΔW_{ce} of the free energy barrier on the water vapor saturation ratio ζ for a marine aerosol of initial radius $R = 97.6$ nm and initial salinity $s = 34.1124$ g/kg. (b) Dependence of ΔW_{ce} on the initial radius R of a marine aerosol of initial salinity $s = 34.1124$ g/kg in a water vapor of saturation ratio $\zeta = 1.0033505$. (c) Dependence of ΔW_{ce} on the initial salinity of a marine aerosol of radius $R = 97.6$ nm in a water vapor of saturation ratio $\zeta = 1.0033505$.

The important role of the surface tension in controlling the hygroscopicity of submicron organic aerosols also transpired from recent experimental studies on the role of OH radicals in the alteration of the activity of submicron organic CCN and their hygroscopic growth.^{17,39–41} It was reported that the aging of submicrometer organic aerosols (triggered by heterogeneous reactions with OH radicals) may significantly alter their activity as CCN via the production of both water-soluble and surface-active species. The former, by dissolving into the droplet core, lower the water activity therein (according to Raoult's law). The latter (which are present on PMA from the very beginning of their existence) reduce the aerosol surface tension which, in turn, reduces the equilibrium vapor pressure over the aerosol thus increasing its hygroscopicity and hence ability to act as a

CNN. The experimental procedure^{17,41} seems to be appropriate to study the Köhler activation⁴² of model marine aerosols, hence one could experimentally verify the predictions of our theoretical model concerning the threshold values of the system parameters necessary for the Köhler activation of marine aerosols. Clearly, as usual, extreme care must be taken in comparing theoretical predictions with experimental results to make sure that both data sets are for similar (if not identical) marine aerosols under identical external conditions.

As clear from Figure 4, for marine aerosols of given size R and salinity s the height of the nucleation barrier disappears at some $\zeta \gtrsim \zeta_K$, where $\zeta_K \equiv \zeta_K(R, s)$ is the threshold value of the saturation ratio necessary for the Köhler activation of the marine aerosols. It is defined via the equation

$$\Delta W_{ce}(R, s, \zeta)|_{\zeta \geq \zeta_K} = 0$$

Likewise, one can define a threshold value $R_K \equiv R_K(s, \zeta)$ of the aerosol radius necessary for the Köhler activation of the aerosol of given salinity s at given vapor saturation ζ via the equation

$$\Delta W_{ce}(R, s, \zeta)|_{R \geq R_K} = 0$$

as well as a threshold value $s_K \equiv s_K(R, \zeta)$ of the aerosol salinity necessary for the Köhler activation of the aerosol of given radius R at given vapor saturation ζ via the equation

$$\Delta W_{ce}(R, s, \zeta)|_{s \geq s_K} = 0$$

Figure 5 illustrates the dependence of ζ_K on the initial size and composition (salinity) of a marine aerosol. In Figure 5a, ζ_K is shown as a function of initial aerosol salinity s at an initial aerosol radius R (each curve corresponds to a constant $R = 0.997 R_0$, R_0 , and $1.003 R_0$ (with $R_0 = 97.6$ nm) from top to bottom), whereas Figure 5b presents ζ_K as a function of R for aerosols of fixed salinity s , with $s = 0.98 s_0$, $1.00 s_0$, and $1.02 s_0$ ($s_0 = 34.1124$ g/kg) for lines from top to bottom. Considering atmospheric conditions of fixed water vapor saturation ratio, one can determine the threshold value R_K of aerosol size necessary for the Köhler activation of aerosols of salinity s . In Figure 5c, R_K is plotted vs s for seven saturation ratios ζ each presented by its own curve ($\zeta = 1.00329$, 1.00331 , 1.00333 , 1.00335 , 1.00337 , 1.00339 , 1.00341 for curves from top to bottom). Every point in the plane R – s represents a marine aerosol with parameters R and s (initial aerosol radius and aerosol salinity). Therefore, a curve of $\zeta = \text{const}$ can be interpreted as the boundary between two regions in the space of parameters R and s corresponding to two qualitatively different types of aerosols. At a given ζ , aerosols belonging to the upper region (above the line $\zeta = \text{const}$) are activated (via Köhler activation) as CCNs and are capable of becoming large droplets that are eventually removed from the atmosphere due to sedimentation/precipitation. On the other hand, aerosols in the lower region (below the line $\zeta = \text{const}$) can not be activated via Köhler-like process; some of them (those very close to the boundary $\zeta = \text{const}$) can still become irreversibly growing droplets via nucleation and become large enough for sedimentation/precipitation.

As clear from the foregoing, even if significant variations of the actual chemical composition of the hydrophobic monolayer of an initial PMA lead to huge variations in the effective equilibrium constants K_1 and K_2 , the activation of the initial PMA as a CCN will be affected *only* by those surfactants which noticeably affect the surface tension of the droplet after chemical reaction 2. Other details/surfactants on the surface of

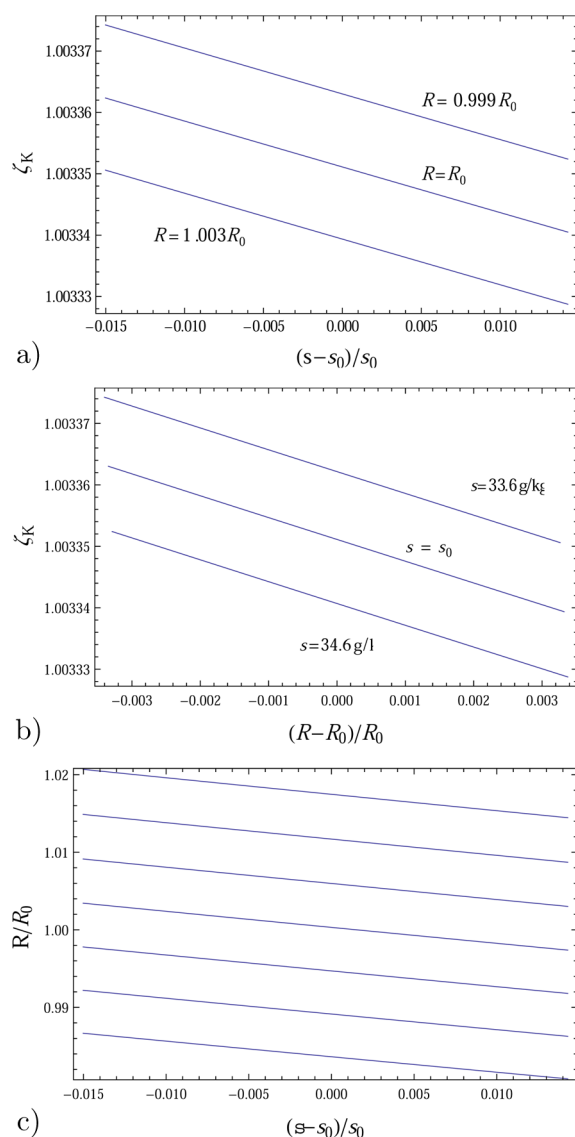


Figure 5. Threshold parameters of the system (initial marine aerosol + vapor/gas medium) for its Köhler activation. (a) Threshold saturation ratio ζ_K as a function of initial aerosol salinity s at a fixed initial aerosol radius R (each curve corresponds to a constant $R = 0.997R_0$, R_0 , and $1.003R_0$, with $R_0 = 97.6 \text{ nm}$, from top to bottom). (b) Saturation ratio ζ_K as a function of R for aerosols of fixed salinity s (with $s = 0.98s_0$, $1.00s_0$, and $1.02s_0$ for lines from top to bottom). (c) Threshold value R_K of aerosol radius vs aerosol salinity s for seven saturation ratios ζ each presented by its own curve ($\zeta = 1.00329, 1.00331, 1.00333, 1.00335, 1.00337, 1.00339, 1.00341$ for curves from top to bottom). The reference quantities $R_0 = 97.6 \text{ nm}$ and $s_0 = 34.1124 \text{ g/kg}$.

the initial PMA can be roughly neglected in estimating the effective equilibrium constants K_1 and K_2 . Similar (although not equivalent) conclusions were drawn from the recent findings⁴³ suggesting that aerosols from diverse sources converge toward similar chemical and physical properties as they age, independent of their original source. As emphasized in ref 44, “this convergence is a great advantage to climate modelers, because it reduces the amount of complexity that must be represented in models that investigate aerosol effects on climate”.

6. CONCLUSIONS

We have studied the thermodynamics of the heterogeneous condensation of water vapor on aqueous aerosols coated with

hydrophobic organic monolayer. The water condensation onto such aerosols becomes possible owing to chemical reactions of the surface layer molecules with atmospheric hydroxyl radicals, oxygen, and other (mostly trace) atmospheric species. These reactions lead to the aging of the hydrophobic coating of the aerosol and render it hydrophilic, thus enabling the aerosol to serve as a cloud condensation nucleus.

A large subset of primary marine aerosols in their initial state (i.e., immediately after formation) can be treated in the framework of an “inverted micelle” model. We have investigated a mechanism whereby water molecules penetrate into the brine core of such a marine aerosol. This becomes possible owing to the formation of RO_2^\bullet (or RO_2^\bullet -like) radicals on the aerosol surface. We have substantiated the necessity of considering the atmospheric processing of the hydrophobic surface monolayer of the marine aerosol and water condensation thereupon as concurrent phenomena, and we have developed a thermodynamic theory thereof.

The very first step of the chemical mechanism of atmospheric aging of organic aerosols may be of several kinds among which two most important are the abstraction of a hydrogen atom from the alkyl tail of a fatty acid or the addition of a hydroxyl radical to alkenes (having unsaturated double bonds ($-\text{CH}=\text{CH}-$)). In the present work, we have considered only the abstraction of a hydrogen atom from a fatty acid by a hydroxyl radical. The second step in this mechanism is the addition of an oxygen molecule to the radical produced on the first step. A surface-bound RO_2^\bullet (or RO_2^\bullet -like) radical formed on the second step, plays a role of an active center for the formation of a cluster of water molecules, which eventually penetrate into the core of the aerosol.

Assuming all the processes to be isothermal-isochoric, we have derived an explicit expression for the free energy of formation of a droplet on a marine aerosol coated with a hydrophobic organic monolayer which is processed by heterogeneous chemical reactions concurrent with water condensation. The free energy of droplet formation as a function of three independent variables of state of a droplet determines a surface (in a 4-dimensional space) that has a form analogous to the free energy surface in a theory of heterogeneous multicomponent condensation; it has a well point and a saddle point if condensation is not barrierless.

To illustrate the proposed thermodynamic model, we have considered hexanoic acid as a hydrophobic organic coating marine aerosols of various sizes and compositions. The numerical calculations show that the number of water molecules in a droplet plays the role of an unstable variable of its state; the dependence of the free energy of droplet formation on that variable is similar to the size dependence of the formation free energy in a theory of heterogeneous condensation. Since the total number of unprocessed surfactant molecules and two kinds of processed ones (surface-bound radicals produced by chemical reactions) is constant, two of these three quantities can be considered as stable variables of state of a droplet.

The numerical results show that the height of the free energy barrier of water condensation on a marine aerosol is very sensitive to the initial parameters of the aerosol (radius and salinity) and is extremely sensitive to the water vapor saturation ratio. For instance, the barrier height decreases from about $100 k_B T$ to about 0 when either the salinity or the (initial) aerosol radius increases by about 0.1%. On the other hand, a similar decrease in the barrier height occurs when the water vapor

saturation ratio increases by about 0.001%! Such small variations in the saturation ratio can easily occur locally (i.e., in the vicinity of a particular aerosol) in the atmosphere due to fluctuations. Therefore, one can conjecture that the formation of aqueous droplets on marine aerosols is most likely to occur in a barrierless way, that is, as a Köhler activation-like process rather than in a fluctuational way (via nucleation).

The proposed model allows one to determine the threshold value of Köhler activation for each of three essential parameters of the initial system “marine aerosol + vapor” (aerosol radius and salinity and water vapor supersaturation) as a function of two others. The numerical results suggest that the process of activation of a marine aerosol depends on the chemical composition of its hydrophobic coating only via the macroscopic surface tension of the evolving aerosol and hardly depends on the microscopic chemical characteristics of surfactant molecules and radicals. Therefore, the theoretical model proposed above is applicable to a very large subset of marine aerosols whereof the hydrophobic coating in the initial state is composed of organic molecules able to participate in the chemical reactions of hydrogen abstraction and oxidation of the resulting radical. This corroborates the previous findings suggesting that one can omit some chemical species of aerosols (and other details of their chemical composition) in models that investigate aerosol effects on climate.

Thus, the proposed thermodynamic model can be useful to improve the current computer models for the distribution of aerosol and cloud particles with respect to their size and chemical composition, especially in a marine boundary layer. An adequate model for such a distribution constitutes a major, necessary component of both regional and global climate models.

■ ASSOCIATED CONTENT

■ Supporting Information

Derivation of eq 3 for the free energy of droplet formation W (in units $k_B T$) as a function of three independent variables of state of a droplet, ν_w, ν_1 , and ν_2 . This material is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

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