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Abstract

The co-adsorption of two atmospheric trace gases on ice is characterized by using, for the first time, Grand Canonical Monte Carlo (GCMC) simulations performed in conditions similar to those of the corresponding experiments. Adsorption isotherms are simulated at tropospheric temperatures by considering two different gas mixtures of 1-butanol and acetic acid molecules, and the selectivity of the ice surface with respect to these species is interpreted at the molecular scale, as resulting from a competition process for the adsorption sites at the ice surface. It is thus shown that the trapping of acetic acid molecules on ice is always favored with respect to that of 1-butanol at low pressures, corresponding to very low coverage of the surface, whereas the adsorption of the acid species is significantly modified by the presence of the alcohol molecules in the saturated portion of the adsorption isotherm, in accordance with the experimental observations. The present GCMC simulations thus confirm that competitive adsorption

effects have to be taken into consideration in the real situations, when gas mixtures present in the troposphere interact with the surface of ice particles.

Gas/ice interfaces are ubiquitous in atmospheric environments, where they influence the local chemistry by acting as trace gas scavengers or as catalysts for heterogeneous surface reactions that may strongly differ from gas phase processes.[1–4] Thus, many laboratory studies have been devoted to the characterization of the trapping properties of various atmospherically relevant molecules, ranging from weakly (e.g., small organic compounds, such as formaldehyde) to very strongly (e.g., inorganic acids, such as HNO_3) interacting species on ice, at tropospheric temperatures.[2,3] Meanwhile, some of these experimental data have nicely been complemented by results coming from numerical simulations, based on the description of the gas/ice interactions at the molecular scale.[5] In these framework, Monte Carlo simulations performed in the grand canonical ensemble (GCMC)[6] have proven to be one of the most suitable modeling approaches,[5,7] because GCMC directly provides the adsorption isotherm, being one of the observables most commonly recorded in the experiments. Thus, maximum surface coverage as well as adsorption energy can be provided on both experimental and theoretical sides for comparison, which allows, for instance, assessment of the interaction potential models used in the simulations.

Laboratory studies of atmospherically relevant adsorption processes have most often been conducted with a single species, and so has also been done by the modeling approaches. However, taking into account the large variety of organic species emitted in the atmosphere, it is also of fundamental importance to characterize how the competition for occupying similar adsorption sites may change the trapping efficiency of the ice surface when different species are simultaneously present.[8] Despite the expected importance of such co-adsorption processes, it is disappointing to note that, as far as we know, only two, relatively old such laboratory studies have been published so far.[8,9] This could, nevertheless, be explained by the corresponding experimental constraints. However, the situation is even worse from the theoretical side, as no study has provided a detailed, molecular-level understanding of the simultaneous adsorption of several compounds on ice.

Again, the GCMC method is an ideal tool to tackle such a challenge, as it has proven to

give a realistic description of the selective trapping of small volatile species in multi-guest clathrates hydrates, in various contexts relevant for astrophysical situations.[10–13] Thus, based on the experience we have acquired by using the GCMC method to characterize, on one hand, the adsorption of one single organic species on ice[5] and, on the other hand, the competition between different species to occupy the cages of clathrate hydrates,[10–13] here we present the results of the first molecular scale simulation study of a competitive adsorption process on ice under tropospheric conditions.

As a first application, we have chosen to investigate the case of mixtures of 1-butanol and acetic acid molecules, i.e., two small, polar, oxygenated organics that are abundant in the atmosphere.[14–16] The choice of these adsorbates is also dictated by the fact that their co-adsorption on ice has previously been investigated in coated-wall flow tube experiments,[8] opening thus the possibility of comparing the present results to the experimental data.

Water molecules have been described by the TIP4P/Ice model,[17,18] whereas the 1-butanol and the acetic acid molecules have been modeled with the flexible AUA4 potential.[19,20] Note that previous simulation studies have shown the relevance of this combination of interaction potential models to accurately describe the behavior of the 1-butanol molecules on ice.[21] Both the TIP4P/Ice and the AUA4 models are defined as sums of pairwise dispersion-repulsion and electrostatic terms, represented by Lennard-Jones (LJ) and Coulomb interactions. Heteronuclear interactions have been calculated in the same way, using the cross LJ parameters determined according to the standard Lorentz-Berthelot combination rules.[22] Analytical tail correction[6] has been applied for the LJ contributions to the interaction potential, while the long-range part of the electrostatic interaction has been accounted for by means of the Ewald summation method.[22]

Ice grains have been simulated by a slab made of 2880 water molecules, arranged in 18 solid layers stacked along the 0001 crystallographic axis (defining the z axis of the system). This ice slab has been placed in a rectangular simulation box of the dimensions of L_x = 35.926 Å, L_y = 38.891 Å, and L_z = 100 Å, in such a way that the slab exhibits two interfaces

in contact with the gas phase, consisting of the 1-butanol and acetic acid molecules, along the z axis. Periodic boundary conditions have been applied along all the three axes. The simulations have been performed using the GIBBS software.[23]

To characterize the adsorption properties of a gas phase containing a mixture of 1-butanol and acetic acid molecules, GCMC runs have been performed, allowing the number of the adsorbate molecules to fluctuate in the simulation box with the value of the total chemical potential μ. For each μ value considered, the number of molecules of each species that are in contact with the ice surface has been determined. This number of adsorbed molecules as a function of μ corresponds, by definition, to the adsorption isotherm for a given composition of the gas phase and a given temperature. For comparisons with experimental data, the results of such simulations have, however, been expressed in terms of pressure instead of chemical potential, using a conversion procedure consistent with the interaction potential models, for the selected compositions of the gas phase, as in our previous works.[13,21,24]

The GCMC simulations have started with a period of equilibration of typically $2-4\times10^8$ Monte Carlo steps. Once the energy of the system and the number of molecules in the basic box started to fluctuate around their equilibrium values, a production run of 2×10^8 Monte Carlo steps has been performed. The 1-butanol and acetic acid molecules have been flexible, while the water molecules have been kept rigid, in accordance with the parametrization of the TIP4P/ice model.[17,18] Thus, in the simulations, the water molecules have only been subject to translational and rotational moves, performed with equal probabilities, while for the 1-butanol and acetic acid molecules, insertion (20 %), deletion (20 %), translation (15 %), rotation (15 %), configurational-biased regrowth (i.e., change of the internal molecular configuration, 15%) and identity swap (i.e., one molecule of a given type is replaced by a molecule of the other type, at the same position, 15%) moves have been attempted.

Our previous works showed that the simulated adsorption isotherms of small alcohols on ice compare very well with experimental data, provided that a small (i.e., about 5 K) temperature shift is considered in the calculations.[7,21] For this reason, the present simulations

have not only been performed at the temperature of the experiments of 228 K, but also at 233 K. However, only the results obtained at this slightly higher temperature are detailed here, because they indeed show an overall better agreement with the experimental data, in particular, when looking at the low pressure part of the adsorption isotherms, as discussed below.

The simulated adsorption isotherms at 233 K are shown in Figure 1 for four various compositions of the gas mixture, corresponding to the gas phase 1-butanol:acetic acid molar ratios of 100:0, 62:38, 25:75, and 0:100. These compositions have been chosen in accordance with the experimental conditions, considering both species separately, and also two mixtures, characterized by gas partial pressure ratio of $P_{\text{acetic acid}} = 3.1 \times P_{\text{1-butanol}}$ and $P_{\text{1-butanol}} = (1.65 \pm 0.15) \times P_{\text{acetic acid}}$.[8] Note that the experimental data at 228 K,[8] extracted from the original publication using the WebPlotDigitizer software,[25] are also reported on Figure 1, for comparisons.

At first, we discuss the adsorption of 1-butanol and acetic acid in the respective neat systems. As seen from Figure 1 (top row), the adsorption behavior of the two molecules is rather similar to each other in the low pressure range, where a rapid increase of their surface concentration, Γ, corresponding to the building up of the adsorption layer at the surface, is observed. It should, however, be noted that the adsorption process starts at much lower pressures for acetic acid than for 1-butanol and, as a consequence, in the low pressure range, up to about 5×10^{-3} Pa, the amount of acetic acid molecules trapped at the ice surface ice is considerably larger than that of the alcohol molecules. The increase of the pressure above 2×10^{-2} Pa only leads to a small variation of Γ for 1-butanol, which is a strong indication of the formation of a stable monolayer.[21] On the other hand, it leads to a continuous increase of Γ for acetic acid due to the adsorption of an increasing amount of molecules at the ice surface up to the completion of the layer, occurring just before the condensation occurs (this condensation is indicated by the sudden vertical jump of the isotherm). Further, in the intermediate pressure range of about $10^{-2} - 1$ Pa, the number of adsorbed alcohol molecules

is always larger than that of acetic acid. The simulated isotherms, calculated at 233 K, agree nicely with the experimental ones, measured at 228 K,[26] especially in the low pressure range, although the simulations tend to somewhat overestimate the amount of adsorbed acetic acid molecules (see Figures 1a and 1b).

The analysis of these results in terms of number density profile, adsorption energy, and orientation of the adsorbed molecules, as in our previous work,[21] allows to draw the following conclusions on the individual adsorption of the two species. At low surface coverage, 1-butanol molecules are adsorbed with their molecular C–C axis being slightly (by about 25°) tilted with respect to the ice surface, the OH group being closer to the water molecules than the methyl group (orientation Alc_A). The distribution of the interaction energy between one adsorbed 1-butanol molecule and the ice surface, U_{alc-w}, exhibits only one, broad, peak, the maximum of which corresponds to about -67 kJ.mol^{-1}, in a nice agreement with the experimental value of the adsorption energy of -67.8 ± 3.8 kJ.mol^{-1}, measured at very low coverage.[26] Meanwhile, the distribution of the interaction energy of one adsorbed 1-butanol molecule with the rest of the adsorption layer, $U_{alc-alc}$, also exhibits one single peak, the maximum of which corresponding to a small value of -4 kJ.mol^{-1}, indicating that the lateral interaction between the adsorbed alcohol molecules is very weak in this low pressure range. By contrast, at pressures corresponding to full coverage, most of the adsorbed molecules tend to move their apolar tail away from, and pointing their polar head towards the ice surface, their molecular axis now being almost perpendicular to the surface (orientation Alc_B). In this new orientation, the U_{alc-w} and $U_{alc-alc}$ distributions of the interaction energies have their maximum around -44 kJ.mol^{-1} and -57 kJ.mol^{-1}, respectively, indicating a strong increase of the lateral interactions between the adsorbed 1-butanol molecules at the expense of their interaction with ice.

When considering the acetic acid molecules, the analysis of the simulation results in the low pressure range, when only a few molecules are adsorbed at the ice surface, indicates that all these molecules adopt almost the same alignment (orientation Ac_α), in which the

C–C axis is tilted by about 30° from the surface normal, the carboxyl group pointing to the water molecules. The corresponding distribution of the interaction energy between one adsorbed acetic acid molecule and the ice phase, U_{ac-w}, is characterized by one single peak, around -73 kJ.mol^{-1}. In this situation, the lateral interaction between adsorbed acetic acid molecules is vanishingly small, indicating that the adsorbed molecules stay isolated from each other. Note that the obtained value of U_{ac-w} agrees well with the experimental value of -73.1 ± 11.7 kJ.mol^{-1}.[26] On the contrary, the analysis of the results obtained at higher pressures, just below the point of condensation, indicates the preference for two different configurations, as seen from the orientational distribution of the molecular C–C axis. It should also be noted that, consistently with this picture, the corresponding energy distributions exhibit two separate peaks. The first of these orientations is, in fact, very similar to Ac_α, observed also at low coverage, while in the second orientation (referred to as Ac_β) the molecular C–C axis lies nearly parallel to the ice surface. This new orientation, Ac_β, can thus be associated with the second peak of the U_{ac-w} distribution, occurring at -38 kJ.mol^{-1}, while the first peak at -68 kJ.mol^{-1} is still associated with configuration Ac_α. The distribution of the lateral interactions, U_{ac-ac}, has its maxima at -22 kJ.mol^{-1} (orientation Ac_α) and -45 kJ.mol^{-1} (orientation Ac_β), indicating that these two orientations differ not only in the interaction with the water molecules, but also in that with the surrounding adsorbed molecules. These results can thus be related to the existence of two different adsorption sites at the ice surface for the acetic acid molecules, as previously evidenced for formic acid molecules.[27] The first ones, at which acetic acid molecules adopt orientations Ac_α, are preferentially occupied at low surface coverage, i.e., at the low pressure range. At higher coverages, adsorption sites of a different type are also progressively occupied (as shown by the increasing slope of the adsorption isotherm) by acetic acid molecules adopting orientation Ac_β.

The situation is clearly different when considering a gas phase that contains a mixture of 1-butanol and acetic acid (blue and green curves in Figure 1). Indeed, while the simulated adsorption isotherms for these mixtures overlap with those of the non-mixed species in the

very low pressure range, they all show a plateau for both molecules at higher pressures. This is a clear indication that, before the condensation occurs, one molecular adsorbed layer is stabilized at the surface of ice, in a broad range of pressures.[5] Moreover, although this monolayer contains co-adsorbed 1-butanol and acetic acid molecules, it is characterized by a significantly lower number of both species than in the non-mixed situation at similar pressures. This shows that the 1-butanol and acetic acid molecules indeed compete for the adsorption sites at the ice surface.

It is worth noting that the simulated behavior of the mixtures agrees, in general, well with the experimental results (grey symbols on Figures 1(e,f)). This agreement is even quantitative when the gas phase contains 25 % of 1-butanol, as evidenced in Figure 1e. On the other hand, the agreement is only qualitative when the gas mixture contains 38 % of acetic acid, as here the simulation results overestimate the amount of adsorbed acetic acid molecules, as already observed also in the non-mixed case. In any case, when the two species can simultaneously be trapped at the ice surface, the maximum number of both molecules that can be adsorbed at the surface is considerably less than in the corresponding non-mixed situations, in accordance with the experimental observations.

The competition between the two co-adsorbed species is more thoroughly investigated at high pressure (i.e., high surface coverage), just before the occurrence of the condensation. Thus, the surface distribution of the XY positions of the carbon atom to which the alcoholic or acidic functional group is attached has been calculated for both species in 10,000 equilibrium sample configurations, and superimposed in the same graph, shown in the top row of Figure 2, for both gas mixtures considered. First, as evidenced by the various spots on these spatial distributions, the entire surface is covered by the adsorbed molecules. Further, 1-butanol and acetic acid molecules clearly prefer to occupy different, well-defined adsorption sites on the ice surface, as indicated by the non-superimposition of the spots corresponding to the different species). It it also seen that the two species are not fully mixed at the ice surface, instead they tend to form well-separated self-aggregates of the same species. To

understand the situation more deeply, the distributions of molecular orientations at the ice surface have also been analyzed at full coverage; the corresponding curves are shown in the bottom row of Figure 2, for the mixed (blue and green curves) and non-mixed (red curves) systems. These distributions clearly show that, within the mixed adsorbed layer, preference for orientation Ac_β nearly vanishes and, as a consequence, acetic acid molecules preferentially adopt orientation Ac_α. The situation is somewhat more balanced for 1-butanol, as both orientations Alc_A and Alc_B are still evidenced when the alcohol molecules are co-adsorbed with acetic acid. However, it is clear that the higher the concentration of 1-butanol is at the ice surface, the weaker is their preference for orientation Alc_A.

The spatial distributions shown in Figure 2 also suggest that the composition of the adsorption layer is different from that of the gas phase, due to the competition in the adsorption process between the 1-butanol and acetic acid molecules. This difference can be more quantitatively characterized by calculating the selectivity of the ice surface for 1-butanol with respect to acetic acid, defined as[12,28]

$$\alpha_{\mathrm{C_4H_{10}O/C_2H_4O_2}} = \frac{N_{\mathrm{C_4H_{10}O}}/N_{\mathrm{C_2H_4O_2}}}{y_{\mathrm{C_4H_{10}O}}/y_{\mathrm{C_2H_4O_2}}} \tag{1}$$

where N_j represents the molar fraction of species j ($j = \mathrm{C_4H_{10}O}$ or $\mathrm{C_2H_4O_2}$) in the adsorption layer, while y_j is the corresponding molar fraction in the gas phase. Thus, following the definition given by Eq. 1, values of $\alpha_{\mathrm{C_4H_{10}O/C_2H_4O_2}}$ larger than 1 indicate that the relative proportion of 1-butanol with respect to acetic acid is larger at the ice surface than in the gas phase, i.e., the adsorption process is selective for 1-butanol. By contrast, $\alpha_{\mathrm{C_4H_{10}O/C_2H_4O_2}}$ values smaller than 1 indicate that the adsorption process is selective for acetic acid.

As shown in Figure 3, the adsorption process remains always selective in favor of the acetic acid molecules (i.e., $\alpha_{\mathrm{C_4H_{10}O/C_2H_4O_2}} < 1$) when 1-butanol molecules are in majority (i.e., 62 %) in the gas phase (green symbols). Nevertheless, it should be noted that the fraction of 1-butanol at the surface increases with pressure up to saturation, as indicated by the increase of $\alpha_{\mathrm{C_4H_{10}O/C_2H_4O_2}}$ up to a more or less constant value. This behavior is even more

pronounced for the other mixture considered here (25 % of 1-butanol). Indeed, in this case, the value of $\alpha_{C_4H_{10}O/C_2H_4O_2}$ remains lower than 1 only up to a threshold pressure, above which the adsorption process, initially being selective for acetic acid, then becomes progressively more favorable to the alcohol molecules, as indicated by the selectivity values larger than 1 at higher pressures. Note that the threshold pressure at which the selectivity becomes larger than 1 roughly corresponds to the pressure at which the adsorption isotherms start to exhibit a plateau (i.e., when a more or less saturated mixed monolayer is formed at the surface).

Summarizing, the results of this first GCMC simulations devoted to the characterization of competitive adsorption clearly show that the trapping of acetic acid molecules is favored at the surface of ice with respect to that of 1-butanol at low pressures, irrespective of the gas phase composition, in a clear accordance with earlier experimental findings.[8] By contrast, at higher pressures, more 1-butanol molecules can be adsorbed, on the expense of the acid molecules, preventing the acetic acid molecules from adopting orientation Ac_β. Moreover, the adsorption process leads to a gradual increase of the 1-butanol mole fraction in the adsorption layer with respect to that in the mixed gas phase, as shown by the increasing value of the ice selectivity for 1-butanol. Similar conclusions are obtained at the two temperatures considered, i.e., 228 K and 233 K. The present results clearly point out that interactions between co-adsorbing gases can play a significant role in their trapping on atmospheric ice particles, and modify their relative molar fractions, especially in the saturated portion of the adsorption isotherm, as already observed in the experiments. Further, they underline that competitive adsorption effects cannot be disregarded when considering real atmospheric situations. The present study also shows that the GCMC method is a powerful and versatile tool for characterizing this competition, provided that accurate interaction potential models are available.

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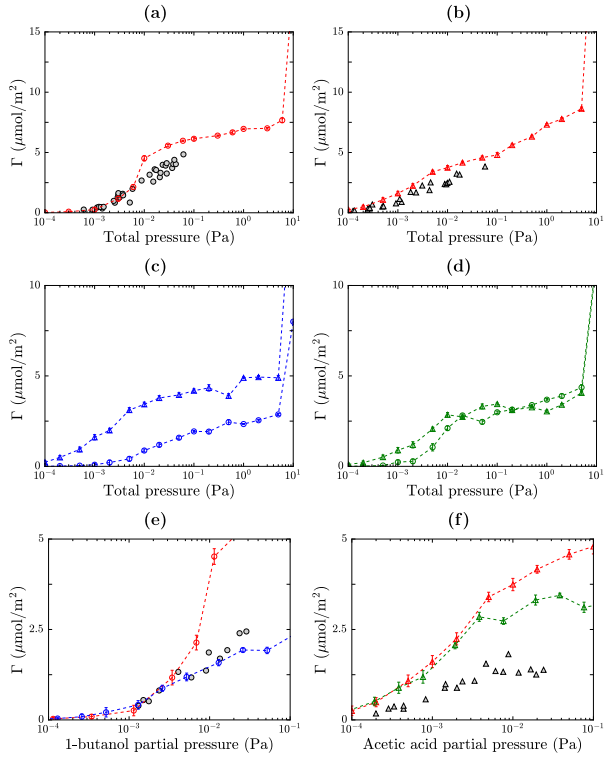

Figure 1: Average number of 1-butanol (circles) and acetic acid (triangles) molecules adsorbed on ice as a function of the pressure (note that the errors bars are smaller than the symbols), as calculated from the present GCMC simulations at 233 K, for various proportions of these two species in the gas phase. Top row: Red curves represent the results obtained for the neat (non mixed) systems. Middle row: Results obtained for the gas phase 1-butanol:acetic acid molar ratios of 62:38 (green curves) and of 25:75 (blue curves). Bottom row : Comparison between results obtained for the non-mixed and the mixed systems, for 1-butanol (left) and acetic acid (right) molecules. Lines connecting the points are only guides to the eye. Comparisons with the experimental data[8] are shown as grey symbols. Note that for the mixtures, these experimental data are unfortunately available for only one species in each case, i.e., butanol for the gas phase 1-butanol:acetic acid molar ratios of 25:75, and acetic acid for the gas phase 1-butanol:acetic acid molar ratios of 62:38.

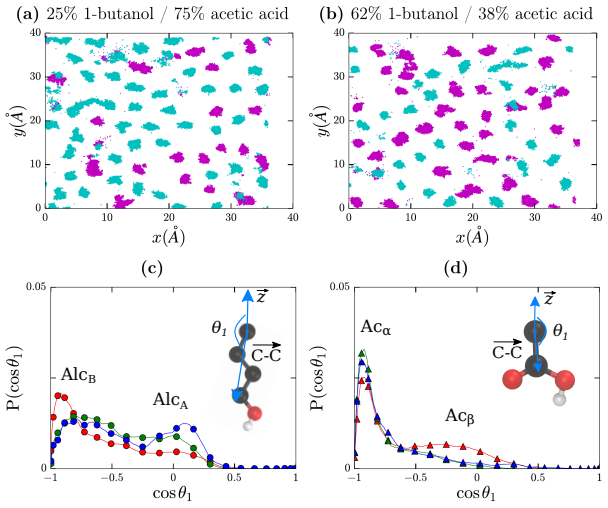

Figure 2: Top row: Surface distribution of the XY positions of the carbon atom of the 1-butanol (purple dots) and acetic acid (blue dots) molecules to which the functional group is attached, for the two compositions of the mixed gas phase investigated here. Bottom row : Distributions of the molecular orientations of the adsorbed 1-butanol (c) and acetic acid (d) molecules, for 1-butanol:acetic acid gas phase molar ratios of 62:38 (green curves) and 25:75 (blue curves). Red curves, shown for reference, correspond to the two non-mixed cases.

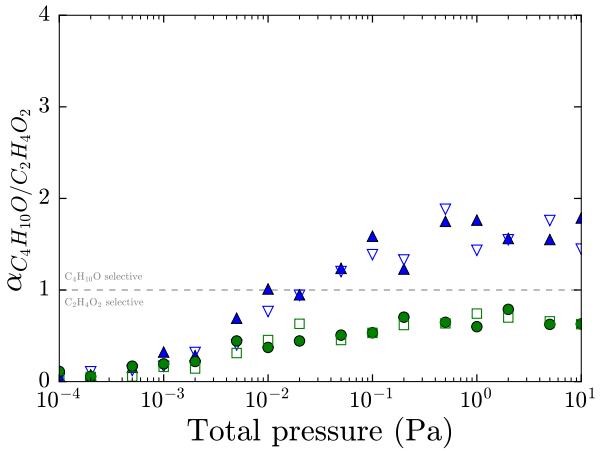

Figure 3: Selectivity of the ice surface as a function of the total pressure, as defined by Eq. 1. Results have been calculated at 228 K (open symbols) and 233 K (full symbols), for the gas phase 1-butanol:acetic acid molar ratio of 62:38 (green symbols) and 25:75 (blue symbols). The limit between acetic acid and 1-butanol selective ice surfaces, corresponding to the selectivity value of 1, is indicated by the horizontal dashed line.

TOC Graphic