

## Effect of adsorption on the uptake of organic trace gas by cloud droplets

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[1] Adsorption can greatly influence the partitioning of organic trace species between the gas and liquid phases. Here we investigate how adsorption of organic species at the air-water interface in clouds can increase the amount of trace gas found in cloud water. For atmospherically relevant cloud surface areas and realistic ranges of adsorption parameters, we show that a significant amount of organic molecules can reside at the cloud droplet surface. Two different physical situations are considered corresponding to the cases where the surfactant is water-soluble and where it is water-insoluble. For both cases, numerical calculations were carried out for a wide range of adsorption parameters, effective Henry's law constants (the former case only), and cloud surface areas. For a soluble surfactant, our calculations show that the "overall" Henry's law constant, which takes into account for both adsorption at the droplet surface and partitioning into the droplet interior, can significantly differ from the standard Henry's law constant. For a moderately soluble species the overall uptake can strongly depend on the surface coverage if the species has a strong affinity for partitioning into the surface layer. Our results also suggest that even insoluble and/or scarcely soluble species can be scavenged by clouds if they are surface-active.

*INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; *KEYWORDS:* uptake of organics, adsorption effect, cloud droplets

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### 1. Introduction

[2] Clouds can significantly alter the chemical composition of the atmosphere through many processes, such as physical uptake, chemical reactions, precipitation, lightning, etc. [Seinfeld and Pandis, 1998; Fleagle and Businger, 1980; Gill et al., 1983]. In this paper we will focus on the physical process of trace gas uptake in clouds.

[3] The process of physical adsorption has a number of important atmospheric implications. First, adsorbed species can participate in heterogeneous chemical reactions [Bertram et al., 2001; Ellison et al., 1999; Abbatt and Waschewsky, 1998], which can greatly influence the chemical composition of the atmosphere. Second, experimental studies of field collected samples indicate that the surface tension of cloud and/or aerosol particles can be lowered, relative to that of pure water [Facchini et al., 1999a, 1999b, 2000; Decesari et al., 2000], which is most likely due to the adsorption of organic molecules at the aqueous solution-air interface. The presence of organic molecules at the aqueous

solution-air interface can influence both the activation process of aerosol particles into cloud droplets [Nenes et al., 2002; Anttila and Kerminen, 2002; Facchini et al., 2000], and the formation of ice in aqueous solutions [Djikaev et al., 2002, 2003; Tabazadeh et al., 2002a, 2002b].

[4] Usually, in atmospheric studies the physical uptake of a trace gas in cloud water is treated by using the Henry's law solubility constant, which linearly relates the trace gas pressure to its bulk concentration in liquid water. However, many observational data exist indicating that the standard Henry's law solubility constant sometimes underestimates the amount of trace gas measured in cloud water, particularly for organic species [Glofelty et al., 1987, 1990; Capel et al., 1991; Schomburg et al., 1991; Sagebiel and Seiber, 1993]. In this paper we suggest that surface adsorption may provide one possible explanation for the underestimation of solubilities predicted by the Henry's law. Specifically, the process of adsorption is not included in the definition of the Henry's law solubility constant. As we show below, for some cases, the number of trace gas molecules adsorbed on the cloud surface may exceed the number of molecules, which are dissolved in the bulk. For such scenarios, the

overall trace gas uptake in cloud water can deviate dramatically from that predicted by Henry's law because this formulation only relates the trace gas pressure to its concentration in the bulk and not on the surface.

## 2. Trace Gas Uptake Without Adsorption

[5] We will first outline the standard procedure for uptake calculations before presenting our model for quantifying the effect of adsorption on this process.

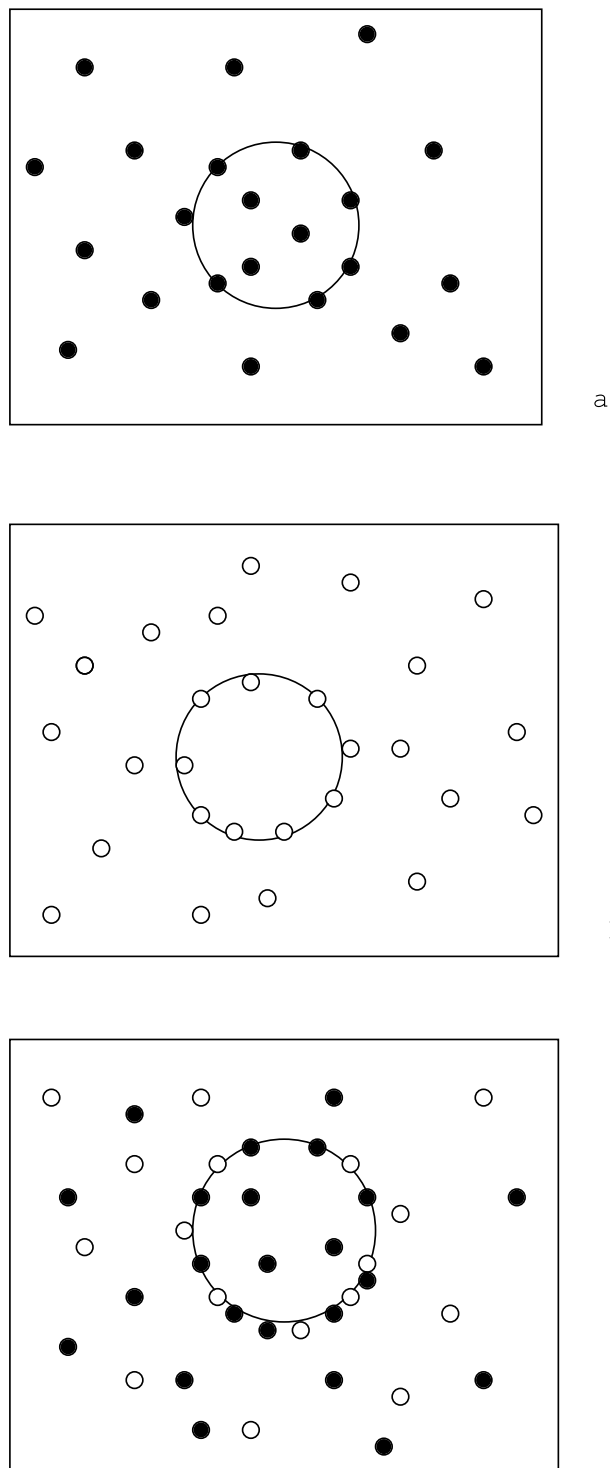
[6] Consider a closed system (a parcel of air) containing fixed numbers of water (component 1) and some trace gas (component 2) molecules, and denote these numbers by  $N_1$  and  $N_2$ , respectively. Denote the volume and temperature of the system by  $V$  and  $T$ . To determine the trace gas uptake by water droplets in equilibrium with the vapor phase, it is necessary to solve the equations reflecting both the equilibrium conditions and mass conservation laws. According to the standard Henry's law,  $c = HP_2$ , where  $c$  is the molarity (moles of solute per liter of solution, units  $M \equiv \text{mol/L}$ ),  $H$  is the Henry's law constant ( $M/\text{atm}$ ), and  $P_2$  is the pressure of the trace gas ( $\text{atm}$ ). The Henry's law, coupled with the mass conservation law with respect to component 2 (trace gas),  $N_2^{vap} + N_2^{sol} = N_2$  allows one to determine  $c$  and  $P_2$ .

[7] In the above procedure it is assumed that the adsorption of trace gas molecules at the liquid-vapor interface is negligible and that these molecules partition either into the liquid or into the vapor. Thus, trace gas molecules adsorbed at the air-water interface are not included in the mass conservation law. In the following section we will investigate how adsorption can increase the trace gas uptake in cloud water. In fact under some conditions adsorption can control the overall magnitude of the uptake process.

## 3. Effect of Adsorption

[8] The effect of adsorption on the overall uptake of a trace gas in cloud water is investigated for two physically different situations. First, the case where the gas molecule is water soluble and surface active (see Figure 1a). In such a system, the partitioning into the interface can occur from both the vapor and liquid phases. Such adsorption can be described by an adsorption isotherm whose parameters are determined by both mechanisms [Donaldson, 1999; Adamson, 1990]. Second, the case where the gas molecule is water insoluble but surface active (see Figure 1b). In such a system, no partitioning into the liquid phase can occur, but the molecule can adsorb at the droplet interface directly from the gas phase. This process is similar to the adsorption of gas molecule onto a solid substrate, but adsorption parameters can certainly be different for a case where the substrate is liquid [Adamson, 1990; Donaldson, 1999]. Thus, these two situations differ in that the mass conservation law should be augmented by different equations in order to take the effect of adsorption into account. It should be noted that in both cases the surfactant molecule is removed from the gas phase and is associated with, but not necessarily dissolved in the liquid phase.

[9] Clearly, in the real atmosphere many trace species can be simultaneously present. Some are water-soluble, while others are water-insoluble (see Figure 1c). Thus, the uptake of one species can, in principle, influence the uptake of



**Figure 1.** Trace gas uptake by a water droplet in different systems. (a) Uptake of water-soluble trace species (filled circles). (b) Uptake of water-insoluble trace species (open circles). (c) Uptake of simultaneously present water-soluble and water-insoluble species.

others. At equilibrium, a multicomponent aqueous droplet may be covered by a thin film of insoluble organics. The transport of water-soluble molecules into and out of the aqueous solution can be impeded or enhanced by factors of

**Table 1.** Parameters  $H$ ,  $H^{\text{eff}}$ ,  $\Gamma_\infty$ , and  $b$  for Some Atmospheric Trace Gases<sup>a</sup>

	$H$ , M/atm	$H^{\text{eff}}$ , M/atm	$\Gamma_\infty$ , cm <sup>-2</sup>	$b$ , M
Acetic acid	$8.8 \times 10^3$	$2.4 \times 10^4$ (5)	$7.5 \times 10^{13}$	1.25
Formic acid	$3.6 \times 10^3$	$6.8 \times 10^4$ (5)		
1-Butanol	54–140		$10.1 \times 10^{13}$	0.12
Methanol	140–230		$9.2 \times 10^{13}$	2.48
Maleic acid	$1 \times 10^9$			
Malonic acid	$2 \times 10^8$			
Formaldehyde (methanal)	2.5	$6.3 \times 10^3$		
Acetaldehyde (ethanal)	1.7–17			
Butyraldehyde (butanal)	5.5–9.6			
Heptanal	2.3–3.7			
Propionic acid	$(2.2-6.2) \times 10^3$		$7.7 \times 10^{13}$	0.351
Acetone	3–35		$6.7 \times 10^{13}$	0.423
Nitric acid	$2.1 \times 10^5$	$3.2 \times 10^9$ (3)	$5 \times 10^{14}$	
Hydrogen Chloride	727	$1.3 \times 10^{12}$ (3)		
Ammonia	62	$1.1 \times 10^6$ (3)	$1.2 \times 10^{14}$	1.37

<sup>a</sup>The numbers in parentheses in column 3 indicate the pH of the solution.

several hundred or more when such films are present [Gill *et al.*, 1983; Mmereki and Donaldson, 2002]. This situation is not considered in the present work but will be the subject of future research.

### 3.1. Uptake of a Water-Soluble Trace Gas

[10] Let us consider a trace gas whose solubility in water is arbitrary but non-zero. At equilibrium, its molecules will be distributed between the vapor mixture, liquid solution, and interface. Thus we have to find three unknowns,  $N_2^{\text{vap}}$ ,  $N_2^{\text{sol}}$ , and  $N_2^{\text{srf}}$ , which give the numbers of molecules of trace gas in the vapor, liquid, and at the interface. To do so *three* linearly independent equations are needed.

[11] First, there is a mass conservation law, relating all the variables:

$$N_2^{\text{vap}} + N_2^{\text{srf}} + N_2^{\text{sol}} = N_2. \quad (1)$$

Next, the Henry's law, providing a relation between  $N_2^{\text{vap}}$  and  $N_2^{\text{sol}}$ . If the solute (trace gas) molecule dissociates in solution, then  $c$  in the Henry's law should be treated as the overall molarity (including dissociated molecules) and  $H$  should be understood as the effective Henry's law constant [Seinfeld and Pandis, 1998]:

$$c = H^{\text{eff}} P_2. \quad (2)$$

Clearly,  $N_2^{\text{sol}}$  should be understood as the overall number of trace gas molecules within the solution. For a solute whose molecules do not dissociate,  $H^{\text{eff}} = H$ . Finally,  $N_2^{\text{srf}}$  can be expressed as a function of either  $N_2^{\text{sol}}$  or  $N_2^{\text{vap}}$  with the help of an adsorption isotherm. The adsorption of many organic species at the interface of their aqueous solutions is often well described by the Langmuir isotherm

$$\Gamma_2 = \Gamma_\infty \frac{c}{b+c}. \quad (3)$$

Here  $\Gamma_2$  is the excess surface coverage of component 2. The parameter  $b$  is related to the rate constants for adsorption and desorption from the surface into the two bulk phases [Donaldson, 1999; Donaldson and Anderson, 1999], and  $\Gamma_\infty$  is the saturation value of  $\Gamma_2$ .

[12] The molarity  $c$  and pressure  $P_2$  can be expressed as  $c = (N_2^{\text{sol}}/N_A)/(V^{\text{sol}}/1000)$  and  $P_2 = N_2^{\text{vap}}kT/(V^{\text{vap}}P_{\text{atm}})$ ,

where  $N_A$  is the Avogadro number,  $k$  is Boltzmann's constant, and the division by  $P_{\text{atm}} = 1013250$  dynes · cm<sup>2</sup>/atm is necessary to obtain the pressure  $P_2$  in units of "atm" (hereafter all other quantities are in CGS units). Thus, Henry's law (2) can be written in the form

$$N_2^{\text{sol}} = H^{\text{eff}} \frac{N_2^{\text{vap}}kT}{P_{\text{atm}}} \frac{V^{\text{sol}}}{V^{\text{vap}}} \frac{N_A}{1000}. \quad (4)$$

[13] Let us assume that the liquid water in the system is monodispersed over  $n^R$  droplets of radius  $R$ . Then, using the Langmuir adsorption isotherm (3), one can obtain

$$N_2^{\text{srf}} = S_n^R \Gamma_\infty \frac{(N_2^{\text{sol}}/N_A)/(V^{\text{sol}}/1000)}{b + (N_2^{\text{sol}}/N_A)/(V^{\text{sol}}/1000)}, \quad (5)$$

where  $S_n^R = 4\pi R^2 n^R$  is the collective surface area of the ensemble of droplets (the appropriateness of one or another adsorption isotherm is discussed in subsection 3.3).

[14] Equations (1), (4), and (5) form a closed system of simultaneous equations in variables  $N_2^{\text{vap}}$ ,  $N_2^{\text{sol}}$ , and  $N_2^{\text{srf}}$ . Its solution can be found analytically:

$$N_2^{\text{vap}} = \frac{Q_1 + \sqrt{4 \times 10^3 (P_{\text{atm}} V^{\text{vap}})^2 b N_2 Q_2 + Q_1^2}}{2Q_2} \quad (6)$$

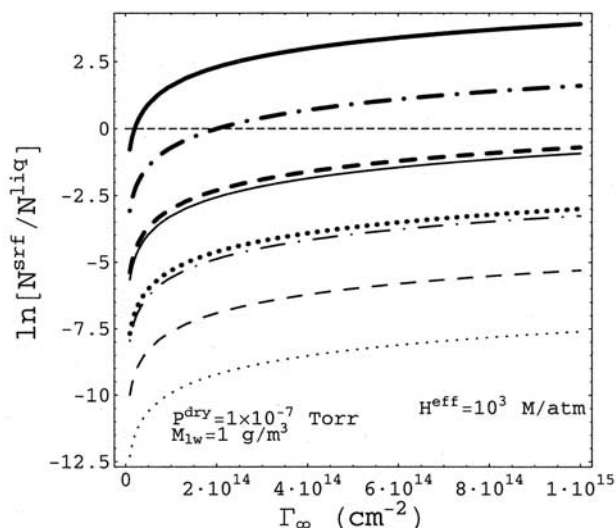
$$Q_1 = H^{\text{eff}} k T P_{\text{atm}} V^{\text{vap}} (10^3 N_2 - 10^3 \Gamma_\infty S_n^R - b N_A V^{\text{sol}}) - 10^3 b (P_{\text{atm}} V^{\text{vap}})^2,$$

$$Q_2 = H^{\text{eff}} k T (H^{\text{eff}} k T N_A V^{\text{sol}} + 10^3 P_{\text{atm}} V^{\text{vap}}),$$

The quantities  $N_2^{\text{sol}}$  and  $N_2^{\text{srf}}$  are then obtained by substituting equation (6) into equation (4) and the result into equation (5).

### 3.2. Uptake of a Water-Insoluble Trace Gas

[15] Many organic species in the atmosphere are only scarcely soluble in water. Thus it is difficult to experimentally determine parameters  $b$ ,  $\Gamma_\infty$ , and  $H^{\text{eff}}$  for such species to use in equation (6). Moreover, many volatile organic



**Figure 2.** Ratio of the numbers of surface and volume located molecules as a function of  $\Gamma_\infty$ . Different line styles correspond to different values of  $b$ : dotted curves represent  $b = 1$  M, dashed  $b = 0.1$  M, dot-dashed  $b = 0.01$  M, and solid  $b = 0.001$  M. The thicker (upper) curves are for  $R = 1$   $\mu\text{m}$  while the thinner (lower) ones are for  $R = 100$   $\mu\text{m}$ .

compounds present in the atmosphere are not water soluble, but may be strong surfactants due to the presence of both highly hydrophobic and hydrophilic structural elements. In fact, a variety of such organic compounds have been identified in atmospheric aerosols [Gill *et al.*, 1983; Dummer *et al.*, 1992; Xiong *et al.*, 1998]. These compounds have natural as well as anthropogenic sources and are mainly aliphatic hydrocarbons with  $C \geq 10$  and their derivatives such as acids, amines, alcohols, aldehydes, ketones, etc. The aliphatics may not have intrinsic surface-active character but can acquire it upon oxidation or amination [Gill *et al.*, 1983]. Among organic surfactants typically found in the atmosphere are alkanes ( $C_{15}$ – $C_{33}$ ), aromatic acids, fatty acids, polycyclic hydrocarbons, humic acids, proteins and protein breakdown products, etc (for a more detailed information on this issue we refer the reader to Gill *et al.* [1983]). The hydrophobic tail of a surface active molecule prevents it from partitioning into water, but such molecules can adsorb at the aqueous solution-air interface owing to their hydrophilic ends. Thus the partitioning between vapor phase and droplets can occur, although there would be no partitioning into the droplet interior. Therefore, the above adsorption model is not appropriate for this case.

[16] In order to take such adsorption into account, the fixed number of trace gas molecules,  $N_2$ , should be distributed between the vapor mixture and aqueous solution-air interface. Thus we need to find only two unknowns, namely,  $N_2^{\text{vap}}$  and  $N_2^{\text{srf}}$ , numbers of molecules of trace gas in the vapor and at the interface, respectively. To do so, the mass conservation law relating these variables,

$$N_2^{\text{vap}} + N_2^{\text{srf}} = N_2, \quad (7)$$

should be augmented by an appropriate adsorption isotherm which describes the adsorption of the trace gas from the

vapor phase onto a liquid water surface. Such adsorption is often (but by no means always) well described by the Langmuir isotherm, that can be written in the form

$$\Gamma_2 = \Gamma_\infty \frac{KP_2}{1 + KP_2}, \quad (8)$$

where the parameter  $K$  is related to the rate constants for adsorption and desorption from the surface into the vapor phase only [Adamson, 1990]. Note that for the adsorption of insoluble species we cannot use the Langmuir adsorption isotherm as given in equation (3), because in this case the concentration of the adsorbate within the solution is zero. For the adsorption of soluble surfactants both equations (3) and (8) can be used, but it is more convenient to use the adsorption isotherm as given in equation (3) (for more detail, see, e.g., Donaldson [1999] and Donaldson and Anderson [1999]).

[17] For the sake of concreteness, let us choose the Langmuir adsorption isotherm to complete our model. Since  $P_2 = kTN_2^{\text{vap}}/V^{\text{vap}}$ , equation (8) can be rewritten in the form

$$N_2^{\text{srf}} = S_n^R \Gamma_\infty \frac{kTKN_2^{\text{vap}}/V^{\text{vap}}}{1 + kTKN_2^{\text{vap}}/V^{\text{vap}}}. \quad (9)$$

[18] Equations (7) and (9) form a closed system of simultaneous equations in variables  $N_2^{\text{vap}}$  and  $N_2^{\text{srf}}$ . Its solution can be found analytically:

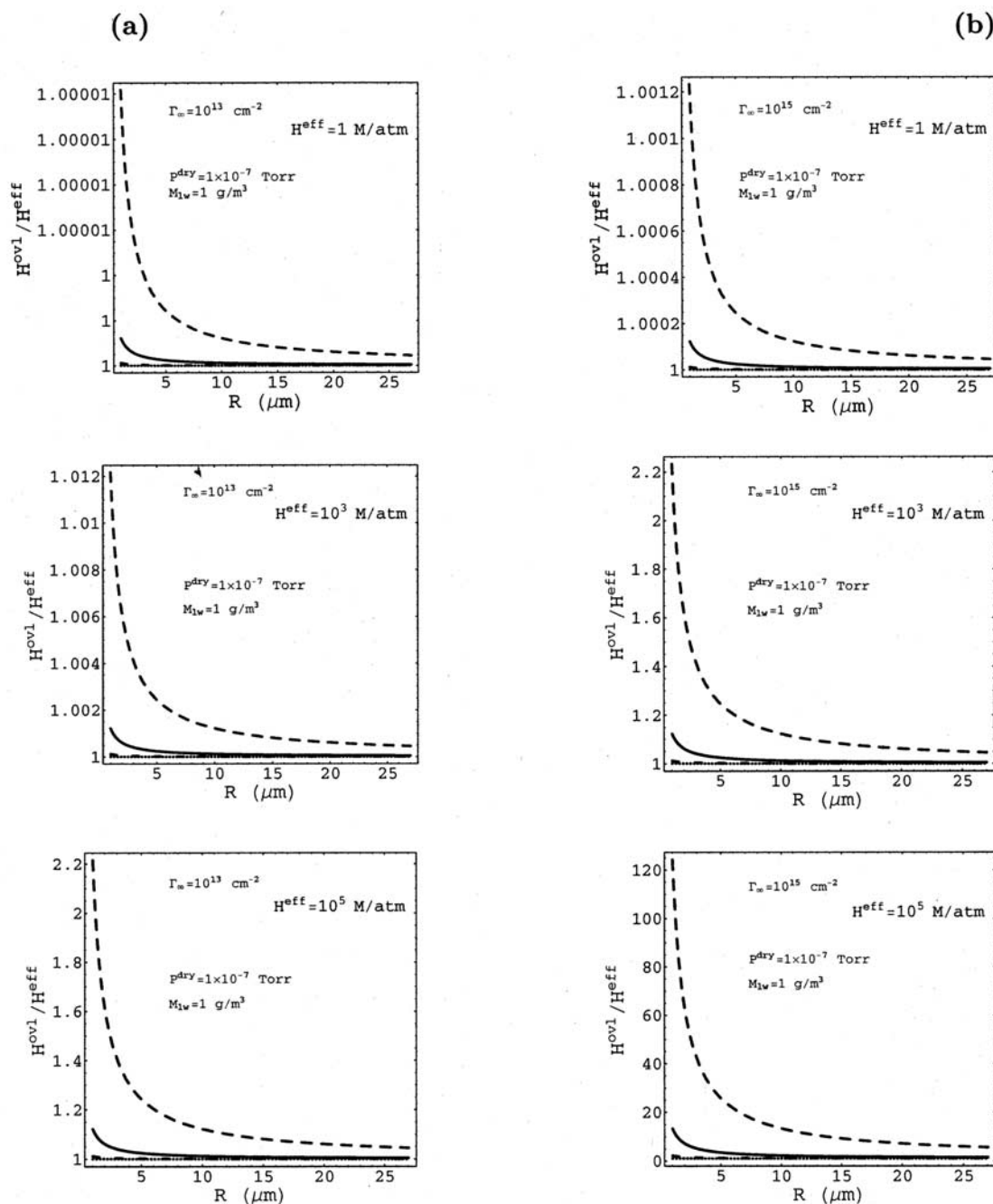
$$N_2^{\text{vap}} = \frac{Q + \sqrt{4kTKN_2V^{\text{vap}} + Q^2}}{2kTK} \quad (10)$$

$$Q = kTK(N_2 - S_n^R \Gamma_\infty) - V^{\text{vap}}.$$

The quantity  $N_2^{\text{srf}}$  is obtained by substituting equation (10) into equation (9).

### 3.3. Generality and Limitations of the Model

[19] As mentioned above, equations (4)–(6) for the vapor-surface-liquid partitioning and equations (9) and (10) for the vapor-surface partitioning are derived for the case where the adsorption of a trace species follows the Langmuir adsorption isotherm. Clearly, if another adsorption isotherm is known to be more appropriate for a given system, equation (3) or equation (8) should be replaced by that isotherm. For example, in the case of a dissociating solute the Langmuir adsorption isotherm should be slightly modified [Adamson, 1990]. Furthermore, the Langmuir adsorption isotherm is inapplicable if the lateral interactions of adsorbate molecules are important, which may be the case, e.g., for “condensed” films [Gill *et al.*, 1983] of long chain hydrocarbons adsorbed on a droplet surface. In this situation the Frumkin adsorption isotherm [Adamson, 1990] is more adequate. On the other hand, many organic compounds that do not contain a “water-soluble” group have been observed [Gill *et al.*, 1983; Baumer and Findenegg, 1982; Hauxwell and Ottewill, 1970] to form “gaseous” films upon adsorption from the vapor phase. In gaseous films the molecules are relatively far apart and are not steeply oriented (as they are in condensed films) but tend to lie flat on the surface [Adam, 1968]. The formation of such films has a multilayer character, and hence the Brunauer-



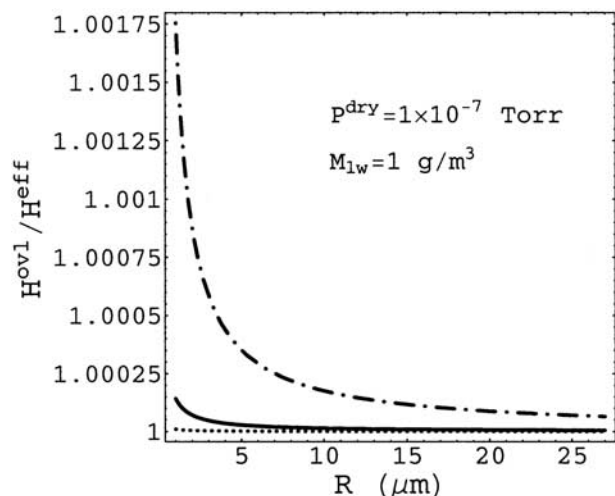
**Figure 3.** Fractional change in the overall Henry's law constant (volume + surface partitioning) as a function of droplet size. In column (a)  $\Gamma_{\infty} = 10^{13} \text{ cm}^{-2}$ , and in column (b)  $\Gamma_{\infty} = 10^{15} \text{ cm}^{-2}$ . The different line styles are for different  $b$ 's, namely: the dotted curve is for  $b = 1 \text{ M}$ , the dot-dashed curve for  $b = 0.1 \text{ M}$ , the solid curve for  $b = 0.01 \text{ M}$ , and the dashed for  $b = 0.001 \text{ M}$ . The values of the effective Henry's law constant and other parameters are given in the panels themselves.

Emmett-Teller (BET) model of adsorption would be more appropriate [Adamson, 1990].

[20] Using any particular adsorption isotherm in the model leads to a set of expressions for  $N_2^{\text{vap}}$ ,  $N_2^{\text{sol}}$ , and  $N_2^{\text{surf}}$  that are specific for that isotherm. Nevertheless, the general procedure of deriving these expressions, as outlined in preceding subsections, will remain unchanged.

[21] Although the above model is designed for a binary system "water + trace species", its generalization to mul-

ticomponent systems is straightforward. Such a generalization is important because in the real atmosphere many organic compounds are simultaneously present. Thus the adsorption of a given species at the droplet surface is influenced by surface contamination resulting from the adsorption of other species. Extending the model to multicomponent adsorption, for every additional trace species we would have to include another set of equations similar to equations (1)–(3) or (7)–(9). An analytical solution will



**Figure 4.** Overall Henry's law constant (volume + surface partitioning) for acetic acid (dot-dashed curve), butanol (solid curve) and methanol (dashed curve). The corresponding parameters are given in the figure panel and Table 1.

probably not always be so simple as for a binary case, due to the fact that the adsorption isotherm will contain the concentrations (in the droplet) or pressures of all trace species. However, numerical solutions of resulting algebraic equations are readily accessible by means of modern computers.

#### 4. Numerical Evaluations

[22] To illustrate the sensitivity of predictions of our model to its different parameters, we carried out numerical evaluations for various  $H^{\text{eff}}$ ,  $\Gamma_{\infty}$ ,  $b$ ,  $K$ , and  $R$ . This would mimic model predictions in different dispersed systems for different volatile and semi-volatile organic species, whose solubility and surface activity in water would be reflected in varying these parameters. The temperature was taken  $T = 298.15$  K. Table 1 compiles the values of these parameters for some species of atmospheric interest. The choice of parameter  $K$  in numerical calculations is discussed below.

[23] The pairs  $H - H^{\text{eff}}$  in Table 1 were taken from *Seinfeld and Pandis* [1998] with indication of pH (between the parentheses) at which  $H^{\text{eff}}$  was evaluated (the effective Henry's law constant depends on pH of the solution). The unpaired values for  $H$  (the Henry's law constant which does not account for dissociation) were taken from R. Sander's web site (<http://www.mpch-mainz.mpg.de/sander/res/henry.html>). The data for  $\Gamma_{\infty}$  and  $b$  were provided by J. D. Donaldson from the University of Toronto (private communication, 2002), except for  $\Gamma_{\infty}$  for nitric acid which was taken from *Hudson et al.* [2002] (some inorganics are included in the table to show how  $H$  and  $H^{\text{eff}}$  can differ from each other). The solubility of a compound decreases with decreasing  $H^{\text{eff}}$ , while its surface activity increases with decreasing  $b$  and increasing  $\Gamma_{\infty}$ .

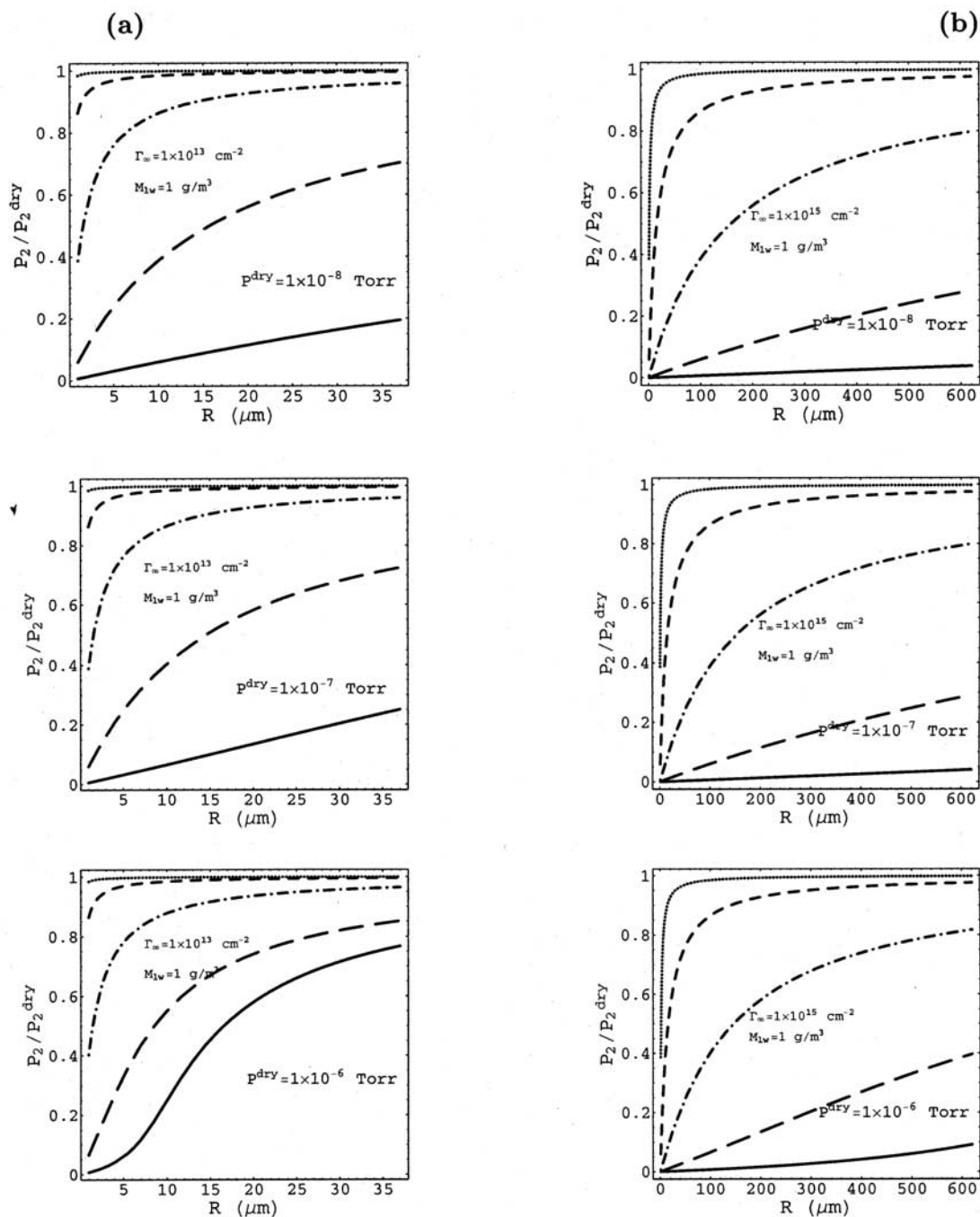
[24] It should be noted that the parameters  $b$  and  $\Gamma_{\infty}$  in Table 1 are given for pure binary systems (water-trace gas). Clearly, in the atmosphere, there are many organic compounds that are simultaneously present in the air. Thus the

adsorption of a given species at the droplet surface in the real atmosphere may not have the same parameters as shown in Table 1, because the droplet surface may be contaminated by other species. Therefore, the above presented models should be further developed to include the possibility of concurrent adsorption [Adamson, 1990], and further experimental work needs to be done to determine adsorption parameters for such systems [Mmereki and Donaldson, 2002].

[25] In our numerical calculations, the vapor and liquid volumes were taken  $V^{\text{vap}} = 10^6$  cm<sup>3</sup> and  $V^{\text{sol}} = 1$  cm<sup>3</sup>, respectively. This gives about 1 g of liquid water per 1 m<sup>3</sup> of air,  $M_{lw} = 1$  g/m<sup>3</sup>, which is rather typical for most clouds although it may be smaller or even greater [Baumgardner et al., 2003] (see below). Results for the adsorption of soluble surfactants are presented in Figures 2–4 while Figure 5 presents results for the adsorption of insoluble surfactants.

[26] Figure 2 shows the logarithm of the ratio  $N_2^{\text{srf}}/N_2^{\text{sol}}$  of surfactant molecules at the surface to that within the droplet interior as a function of parameter  $\Gamma_{\infty}$  in the range from  $10^{13}$  to  $10^{15}$  cm<sup>-2</sup>. The horizontal dashed line shows where  $N_2^{\text{srf}} = N_2^{\text{sol}}$  (for more detail see the figure panel and caption). The relative number of surface-located molecules (i.e., the ratio  $N_2^{\text{srf}}/N_2^{\text{sol}}$ ) decreases by two orders of magnitude when the droplet radius increases from  $R = 1$  μm to  $R = 100$  μm for a fixed set of adsorption parameters. This occurs due to an increase in the surface-to-volume ratio of droplets with decreasing size. On the other hand, as expected, at a fixed  $R$  the ratio  $N_2^{\text{srf}}/N_2^{\text{sol}}$  increases with increasing  $\Gamma_{\infty}$  and decreasing  $b$ . Surprisingly, the  $N_2^{\text{srf}}/N_2^{\text{sol}}$  ratio is quite insensitive to the Henry's law constant,  $H^{\text{eff}}$ : the lines would remain nearly unchanged for  $H^{\text{eff}}$  ranging from 1 to  $10^{10}$  M/atm (the calculations shown are for  $H^{\text{eff}} = 10^3$  M/atm). Furthermore, the predictions of the model are not sensitive to  $P_2^{\text{dry}}$ , the trace gas pressure in the dry air parcel, at least under typical atmospheric conditions, where the trace gas pressure may vary in the range from  $10^{-8}$  to  $10^{-6}$  torr. According to *Singh et al.* [2001] the total pressure of organic trace species in the atmosphere hardly exceeds  $2 \times 10^{-6}$  torr, with methanol partial pressure being by far the largest of all oxygenated organics.

[27] In order to make a comparison between the predictions of our (modified) uptake model and those of the standard model (without adsorption), we calculated the ratio of the overall (including adsorption) and standard (bulk) effective Henry's law constants,  $H^{\text{ovl}}/H^{\text{eff}}$ . The quantity  $H^{\text{ovl}}$  was calculated by using the expression  $H^{\text{ovl}} = P^{\text{new}}/c^{\text{ovl}}$ , where  $P^{\text{new}}$  is the pressure predicted by our model and  $c^{\text{ovl}} = 1000 * (N_2^{\text{sol}} + N_2^{\text{srf}})/(N_A V^{\text{sol}})$ . Figure 3 shows the dependence of  $H^{\text{ovl}}/H^{\text{eff}}$  on the droplet radius  $R$ . The values of the effective Henry's law constant, adsorption parameters, and other details are given in the figure panels and caption. The extreme case  $H^{\text{eff}} = 0$  and  $b = 0$  would correspond to an insoluble surfactant. The specific curves (according to parameters given in Table 1) for acetic acid, butanol, and methanol are shown in Figure 4. As clear, the lines in all the panels converge to 1 with increasing  $R$ . Thus, for large droplets the overall partition coefficient,  $H^{\text{ovl}}$ , is quite insensitive to adsorption parameters and coincides with the standard value,  $H^{\text{eff}}$ . However, for small droplets the effective partition coefficient strongly depends on adsorption parameters and may significantly differ from



**Figure 5.** Reduction in the pressure of a trace gas of insoluble surfactant as a function of droplet size. In column (a)  $\Gamma_{\infty} = 10^{13} \text{ cm}^{-2}$ , and in column (b)  $\Gamma_{\infty} = 10^{15} \text{ cm}^{-2}$ . The different colors correspond to the different values of  $K$ , namely:  $K = 1.7 \times 10^3 \text{ Torr}^{-1}$  for the dotted curve,  $K = 1.7 \times 10^4 \text{ Torr}^{-1}$  for the short-dashed curve,  $K = 1.7 \times 10^5 \text{ Torr}^{-1}$  for the dot-dashed curve,  $K = 1.7 \times 10^6 \text{ Torr}^{-1}$  for the long-dashed curve, and  $K = 1.7 \times 10^7 \text{ Torr}^{-1}$  for the solid curve.

$H^{\text{eff}}$ . Besides, for a given set of adsorption parameters the overall Henry's law constant  $H^{\text{ovl}}$  strongly depends on the droplet size (this can be explained by the variation of the surface-to-volume ratio of a droplet with variation of its size). These two features could not have been captured within the framework of the standard uptake models, where surface effects are simply neglected.

[28] Finally, Figure 5 illustrates the adsorption behavior of an insoluble surfactant. The plots show  $P_2/P_2^{\text{dry}}$ , the ratio

of the trace gas pressure in the dispersed system to its "dry" pressure (in the absence of water droplets) as a function of droplet radius  $R$ . The adsorption parameters and other details are given in the panels and caption of Figure 5. The  $K$  values considered ensure that the inequality  $KP_{2e} \gg 1$  (with  $P_{2e}$  being the equilibrium vapor pressure of trace gas) holds for most volatile organic compounds of interest. This inequality should hold because if  $P_2 = P_{2e}$ , the trace gas would be in equilibrium with its pure liquid state. Therefore

a monolayer coverage should be expected to exist at the water surface under such a pressure, i.e.,  $\Gamma \simeq \Gamma_\infty$  at  $P_2 \simeq P_{2e}$ , which leads to the condition  $KP_{2e} \gg 1$ . As clear, even for large droplets the trace gas depletion is quite sensitive to the adsorption parameters  $K$  and  $\Gamma_\infty$ . Also, for a given set of adsorption parameters, the trace gas depletion depends strongly on the droplet size (again, this is seemingly due to the variation of the surface-to-volume ratio of a droplet with  $R$ ). Right panels (b) in Figure 3 show the whole range of possible droplet radii (the total liquid volume is  $1 \text{ cm}^3$ ). Even one single water droplet of radius  $620 \text{ }\mu\text{m}$  can strongly deplete a trace gas of insoluble surfactant, having the adsorption parameters  $\Gamma_\infty \approx 10^{15} \text{ cm}^{-2}$  and  $K \gtrsim 5 \times 10^3 \text{ torr}^{-1}$ . The existing models of trace gas uptake by clouds are intrinsically unable to capture any of these features because they neglect the process adsorption.

[29] In accordance with Figures 3 and 4, for droplets with  $R \lesssim 1 \text{ }\mu\text{m}$  the effect of adsorption on the uptake of a soluble species can become significant for  $b \lesssim 1 \text{ M}$ . The smaller  $H^{\text{eff}}$  is, the more stringent the surface activity requirement is (i.e., the smaller  $b$  is required). Furthermore, the adsorption effect can be important for  $\Gamma_\infty \gtrsim 10^{12} \text{ cm}^{-2}$  provided that the corresponding  $b$  is small enough. If the liquid water content is reduced to  $M_{lw} = 0.1 \text{ g/m}^3$  (results not shown in figures), the effect of adsorption becomes weaker, especially for ensembles of large droplets, but remains significant for  $H^{\text{eff}} \gtrsim 10^3 \text{ M/atm}$  and  $b \lesssim 0.1 \text{ M}$ . Figure 5 shows that for droplets with  $R \lesssim 1 \text{ }\mu\text{m}$  the effect of adsorption on the uptake of an insoluble surfactant can become important when  $K \gtrsim 10^4 \text{ Torr}^{-1}$  and  $K \gtrsim 10^3 \text{ Torr}^{-1}$  for  $\Gamma_\infty \simeq 10^{13} \text{ cm}^{-2}$  and  $\Gamma_\infty \simeq 10^{15} \text{ cm}^{-2}$ , respectively. For these ranges of adsorption parameters, reducing the liquid water content to  $M_{lw} = 0.1 \text{ g/m}^3$  (results not shown in figure) has a negligible effect on the uptake.

[30] As mentioned above, in the real atmosphere many trace species are simultaneously present. Therefore, their uptake by cloud droplets occurs as a concurrent process conditioned by all compounds. For example, according to Gill *et al.* [1983], Dumer *et al.* [1992], and Xiong *et al.* [1998], the transport of molecules into and out of the aqueous solution is impeded by factors of several hundred or more when organic films are present. Recently, Mmereki and Donaldson [2002] have also reported an enhanced adsorption of pyrene at the hexanoic acid-coated water surface, even with sub-monolayer coverages of hexanoic acid. One can expect to observe a similar adsorption effect for many organic molecules present in the atmosphere.

## 5. Concluding Remarks

[31] We have presented a new model for the uptake of atmospheric trace gases by water droplets in clouds. In our model, the gas adsorption at the droplet-air interface is taken into account. We have investigated how the adsorption of organic molecules at the air-water interface in clouds can increase the amount of trace species found in cloud water. We have shown that for atmospherically relevant cloud surface areas and realistic ranges of adsorption parameters a significant fraction of organic molecules can reside at the surface of cloud droplets. Two different physical situations have been studied, corresponding to the cases where the trace gas is water-soluble and where it is water-insoluble. To

analytically describe the adsorption phenomenon, the adsorption isotherm for a given system needs to be known. This can be written in terms of solution composition if the surfactant is water-soluble, or in terms of the pressure if the surfactant is water-insoluble. For the sake of illustration, we have carried out numerical calculations for a wide range of adsorption parameters, effective Henry's law constants (the former case only), and cloud surface areas using the Langmuir adsorption isotherm. For a soluble surfactant, our calculations show that the "overall" Henry's law constant, which takes into account for both adsorption at the droplet surface and partitioning into the droplet interior, can significantly differ from the experimental Henry's law constant. For an insoluble surfactant, our results suggest that an organic trace gas can be strongly depleted by clouds due to mere adsorption onto cloud droplet surfaces.

[32] Both adsorption models that we have presented above are applicable only to pure binary systems (water-trace gas). In the real atmosphere, many types of organic compounds are simultaneously present. Therefore the adsorption of one species at the droplet surface is likely to occur as concurrent adsorption at the surface contaminated by other surfactant(s). Contaminants can either enhance or impede the adsorption of other species. Thus, further work needs to be done to include the possibility of multicomponent adsorption, and more experimental work is needed to determine the corresponding adsorption parameters.

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