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Influence of the ice growth rate on the incorporation of gaseous HCl

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Abstract

Ice crystals were grown in the laboratory at −15°C, at different growth rates and in the presence of a partial pressure of HCl of 1.63×10^{-3} Pa, to test whether the ice growth rate influences the amount of HCl taken up, X_{HCl}, as predicted by the ice growth mechanism of Domine and Thibert (1996). The plot of HCl concentration in ice as a function of growth rate has the aspect predicted by that mechanism: X_{HCl} decreases with increasing growth rate, from a value that depends on thermodynamic equilibrium to a value that depends only on kinetic factors. The height of the growth steps of the ice crystals is determined to be about 1.5 nm from these experiments. We discuss that the application of these laboratory experiments to cloud ice crystals and to snow metamorphism is not quantitatively possible at this stage, because the physical variables that determine crystal growth in nature, and in particular the step height, are not known. Qualitative applications are attempted for HCl and HNO_3 incorporation in cloud ice and snowpack crystals.

1. Introduction

The understanding of snow composition is crucial for numerous scientific fields such as ice core inversions (Domine et al., 1995; Legrand and Mayewski, 1997), air-snow interactions (Domine and Shepson, 2002), hydrology (Tranter et al., 1986; Cragin et al., 1993; Domine and Thibert, 1995) and ecology (Crittenden, 1998). Snow on the ground undergoes metamorphism, a set of physical processes which includes sublimation-condensation cycles that lead to changes in the size and shapes of snow crystals (Colbeck, 1982; Domine et al., 2003). These changes are caused mostly by the thermal gradient in the snow, that lead to water vapor fluxes, which in turn entrain gases dissolved in the crystalline lattice of the snow crystals or adsorbed on their surface. Many studies monitoring the composition of the snow after deposition have observed significant changes in the concentration of gases contained in the snow phase (see for example Hutterli et al., 2002 and Perrier et al., 2002 for HCHO; Jacobi et al., 2002 for HCHO and H_2O_2; Domine et al., 1995 for HCl; Rothlisberger et al., 2002 for HNO_3). Many processes can be invoked to explain those changes: solid state diffusion out of snow crystals as suggested by Perrier et al. (2002) for HCHO, release during metamorphism as suggested by Nakamura et al. (2000) in the case of HNO_3, photolysis as suggested by Jones et al. (2001) for HNO_3, and the release of desorbed species because of the decrease in the specific surface area of snow during metamorphism, as suggested theoretically for acetone by Domine et al. (2002) and for acetaldehyde from measurements by Houdier et al. (2002).

The purpose of this work is to contribute to the understanding of the role of metamorphism in the change in composition of snow crystals. The mole fraction of gases dissolved will be the result of kinetic and thermodynamic processes. Domine and Thibert (1996) have proposed a physical mechanism to predict the concentration of a dissolved gas as a function of the growth rate of the ice crystal and of the intrinsic properties of the gas. According to this mechanism, at very fast growth rates, the gas mole fraction in ice, X_{gas}, is predicted by condensation kinetics, and is then X_{kin}:

$$X_{kin} = \frac{P_{gas}\alpha_{gas}}{P_{\mathrm{H2O}}\alpha_{\mathrm{H2O}}}\sqrt{\frac{M_{\mathrm{H2O}}}{M_{gas}}} \tag{1}$$

where P is the partial pressure, α is the mass accommodation coefficient (also called “sticking” coefficient) on the ice surface, M is the molar mass, and the subscripts H_2O and *gas* pertain to water and the dissolved gas, respectively.

At very slow growth rates, X_{gas} is determined by the thermodynamics of the solid solution of the gas in ice, that predict $X_{eq}=f(T, P_{gas})$, where T is temperature and X_{eq} is the mole fraction of the gas dissolved in ice at thermodynamic equilibrium. This is known for HCl and HNO_3 (Thibert and Domine, 1997, 1998). For HCl, this relationship is:

$$X_{\mathrm{HCl}} = 6.1310^{-10} e^{\left(2806.5/T\right)} \left(P_{\mathrm{HCl}}\right)^{1/2.73} \tag{2}$$

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with T in Kelvin and P_{HCl} in Pa.

In many cases, however, both kinetic and thermodynamic factors contribute to X_{gas}. Domine and Thibert (1996) mentioned that under atmospheric conditions, the growth of ice crystal is a discontinuous process that takes place by the propagation of new growth steps nucleating at crystal edges. Each new step, of thickness h, is then formed with a composition X_{kin} determined by Eq. (1). Since this is out of equilibrium with the atmosphere, solid state diffusion of the gas in the ice lattice will take place to drive the composition towards X_{eq}. Equilibration can proceed during a duration τ, after which a new ice layer is deposited, isolating the lower layer from the atmosphere and blocking diffusion from the gas phase. The resulting X_{gas} value is then given by:

$$X_{gas} = \left(X_{kin} + {}^{(X_{eq} - X_{kin})}\!\big/_{h}\right) \int_0^h erfc\left(x \Big/ 2\sqrt{D_{gas}\tau}\right) dx, \tag{3}$$

where D_{gas} is the diffusion coefficient of the gas in ice and *erfc* is the complementary error function. In the case of HCl, under most tropospheric conditions $X_{kin} \ll X_{eq}$, and Eq. (3) thus predicts that at slow growth rates, X_{HCl} will be higher than at fast growth rates. Thus, in a snowpack undergoing intense metamorphism driven by a strong temperature gradient leading to fast crystal growth (Domine et al., 2003), X_{HCl} of snow should be lower than in a snowpack subjected to a low temperature gradient, where crystal growth will be slow. In clouds, where crystal growth is almost always faster than in the snowpack, this predicts that HCl concentration will be mostly determined by kinetic factors, as observed by Domine and Thibert (1996).

In this paper, we describe laboratory experiments where we grew ice crystals at several growth rates in the presence of a fixed P_{HCl}. HCl was chosen because its solid solution with ice has been extensively studied, and its diffusion coefficient in ice is known (Thibert and Domine, 1997). We measured X_{HCl} and used the data to test the mechanism of Domine and Thibert (1996). The data can also be used to determine h, the height of the growth steps in our experimental system.

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2. Experimental methods

Gas mixtures of H_2O and HCl diluted in N_2 were flowed into a crystallization tube as shown in Figure 1. The upstream bubbler was filled with ultra pure water (resistivity >18 MΩ.cm), and the N_2 flow through that bubbler was adjusted to obtain the desired supersaturation in the crystallization tube, and this controlled the growth rate. Supersaturation values were determined from the data of Marti and Mauersberger (1993). HCl came from two commercial mixtures (Air Liquide) of HCl in N_2 of molar concentrations 9.9 and 45.6 ppm. These concentrations were verified by flowing known amounts of mixture in the downstream bubbler, followed by determination of the Cl^- content by ion chromatography. Under the conditions used, the HCl in the bubbler water remained very unsaturated relative to the gas phase (Fritz and Fuget, 1956), so that all the HCl was effectively trapped in the bubbler. The crystallization tube had an internal diameter of 5 cm and the gas mixture flowed into it at a rate of 1.5 L/minute through a glass sphere 1.5 cm in diameter (Fig. 1) where 20 holes had been made to maximize mixing in the tube. The maximum mass of ice that could form was predicted from the supersaturation and the gas flow rate, and this was equal to the measured mass of ice, within 15%. Two methods were used to retrieve the solid solution of HCl in ice formed: melting in the tube followed by analysis, and scraping of the inside of the tube in a cold room at −15°C followed by analysis by ion chromatography using a Dionex 4000i instrument located in a clean room. Both methods produced similar results. Numerous tests and blanks were performed to identify and minimize possible sources of contamination.

Blanks were run with no HCl, under flow conditions similar to the experiments with HCl. Although Cl^- was below detection limit ($0.5\ 10^{-9}$ mole fraction, hereafter 0.5 ppb) in the water poured into the bubblers, the ice did have a measurable amount of Cl^-, that depended on its growth rate. The source of the contamination was not clearly identified. Tests showed the N_2, obtained from evaporating liquid N_2, to be very clean. We rather believe that it is caused by HCl released from tubing or from flowmeters, that are difficult to clean perfectly, as HCl readily sticks to surfaces. In any case, the blank

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values were significantly lower than the signal, and were simply subtracted from the experimental values.

Before each experiment, the gas lines and the crystallization tube were conditioned by flowing the experimental mixture through them at room temperature for at least one hour.

3. Results and discussion

Since our objective was to study the impact of the ice growth rate on HCl incorporation, 10 experiments were performed by varying the water supersaturation, and hence the ice growth rates, while maintaining total flow, temperature, and P_{HCl} constant. Results obtained at T=−15°C, for $P_{\mathrm{HCl}}=1.67\times10^{-3}$ Pa are shown in Table 1 for supersaturations of 15, 40, and 82.5%. Under those conditions, the equilibrium HCl mole fraction in ice is X_{eq}=3120 ppb (Thibert and Domine, 1997). The values obtained after subtracting blank values are between 11 and 155 ppb, much lower than X_{eq}, indicating that kinetic processes play an important role in determining X_{HCl}. Figure 2 shows a plot of X_{HCl} as a function of supersaturation.

Based on the 10 experiments performed at 3 P_{HCl} values, the curve has the aspect predicted by Domine and Thibert (1996). At high supersaturation, the curve tends asymptotically towards a value around 10 ppb, which is X_{kin} according to the mechanism tested here. At low supersaturation X_{HCl} increases, presumably towards X_{eq}, but the growth rates needed to test this in more detail are too slow to be practically achieved.

The data at fast growth rates allow the estimation of $\alpha_{\mathrm{HCl}}/\alpha_{\mathrm{H2O}}$ on ice from Eq. (1). We obtain a value of 0.0014. This appears much lower than expected from literature values. The parameter α_{HCl} has been measured in the laboratory around −80°C, and values between 0.1 and 1 have been found (Leu et al., 1988; Hanson and Ravishankara, 1992). Similarly, α_{H2O} is in the range 0.1 to 1 (Haynes et al., 1992 and references therein). Domine et al. (1995) and Domine and Thibert (1996) deduced

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from field measurements that values α_{HCl}=0.2 and α_{H2O}=0.5 were adequate to explain observations in Greenland snow at −15°C. This leads to $\alpha_{HCl}/\alpha_{H2O}$=0.4, a factor of about 300 greater than found here.

This apparent discrepancy does not, however, invalidate our results. Unlike the rate coefficient of a gas phase reaction which has a universal value, the sticking coefficient of a gas on a surface depends on the state of the surface and in particular on it defect density, on the nature of the surface itself (e.g. basal vs. prismatic), on the growth mechanism of the crystal, and on supersaturation. The variables influencing sticking coefficients on solid surfaces are so numerous that one should even wonder whether attempting to reduce their description to a single value has any meaning, even though it is convenient in models. In the case of ice, growth under atmospheric and most laboratory conditions take place by 2-D layer nucleation at crystal edges (Frank, 1982; Nelson and Knight, 1998; Libbrecht, 2003a) which means that there is a critical supersaturation necessary for the onset of growth and that α_{H2O} will depend on the supersaturation. Libbrecht (2003a) showed this in detail and measured α_{H2O} values between 0.001 and 0.4, depending on the crystal face and supersaturation. In a further paper, Libbrecht (2003b) even suggests that at fast growth rates at −15°C, under conditions similar to those of our study, the growth mechanism would change. Flat crystal faces would not be present anymore, the tip of dendritic crystals would be curved, nucleation would be at the center of faces, not at the edges, and the sticking coefficient on the fast growing prism face would increase to 1. Since α_{H2O} is governed by surface structure and processes, it appears reasonable that α_{HCl} could then also be affected by the same variables that affect α_{H2O}, and possibly in a different way. α_{HCl} could thus be different from values measured or inferred under conditions other than those found here. The ratio $\alpha_{HCl}/\alpha_{H2O}$ could then show large variations depending on experimental conditions.

To sum up this point, we believe that the value $\alpha_{HCl}/\alpha_{H2O}$=0.0014 that we find, although it appears lower than could be expected from a few other studies, is not necessarily unreasonable and could merely reflects the physics of ice growth under our

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conditions.

Our data can also be used to derive the height of the ice growth step, *h*, using our measurements at 15% supersaturation, where kinetic and thermodynamic processes both play a significant role, and where Eq. (3) therefore applies. At −15°C, the diffusion coefficient of HCl in ice is about 2×10^{-12} cm^2/s (Thibert and Domine, 1997). Other values have been proposed for this parameter, but Thibert and Domine (1997) and subsequently Domine and Xueref (2001) have explained in detail why those other values are highly questionable. We also need to know τ, the time during which a layer just deposited remains in direct contact with the atmosphere. This is related to the growth rate v, and to h by τ=h/v, so all we now need to know to solve Eq. (3) for h is the growth rate v.

The growth rate can be calculated from the supersaturation and α_{H2O}, but this last variable is not known for our conditions. It can also be inferred from the mass of ice that was retrieved and the surface area over which it grew. Finally, the maximum ice mass that could form can simply be determined from mass balance calculations. For the experiments at 15% supersaturation, the growth rate found was about 1 μm/s. This value is also deduced from the mass balance calculations, assuming all excess molecules condense as ice. This is consistent with Libbrecht's suggestion that at fast growth rate (≥5% supersaturation, according to Libbrecht), α_{H2O} is close to unity.

Knowing v, we solved Eq. (3) for h and found h=1.5 nm. Since at −15°C, ice grows almost exclusively along the *a* direction (prism face) and the unit cell in that direction has a dimension of about 0.45 nm (Hobbs, 1974), each growth step has average an thickness of about 3 unit cells. This is much less than found in early growth experiments. For example, growth on covellite surfaces yielded step heights of 20 to 100 nm (Hallett, 1961). However, most of these early studies focused on the basal face, and again, crystal growth parameters are influenced by numerous variables such as growth rate, the nature of the surface on which crystals are grown, the crystallographic face and the defect density, so that there is no reason why values of h found in one study should be reproduced in another study using different experimental conditions.

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Santachiara et al. (1995) also studied the incorporation of HCl in ice crystals growing by the Bergeron mechanism from water droplets containing HCl in a diffusion chamber at −13°C. They found X_{HCl} values up to 3000 ppm, much higher than the maximum thermodynamic solubility (Thibert and Domine, 1997). However, they induced ice nucleation by introducing "a small metal bar cooled in liquid nitrogen" in their chamber, creating a cold spot. It then seems that neither the crystal growth temperature, nor P_{HCl} can be determined, and it is not possible to compare their results with ours.

Diehl et al. (1995) grew ice crystals from water vapor at −15°C, with a supersaturation estimated at about 15% in a diffusion chamber, and in the presence of HCl. Their lowest P_{HCl} was about 5×10^{-3} Pa, and the resulting X_{HCl} was about 200 ppb. Besides P_{HCl}, their conditions are similar to our experiments at 15% supersaturation, and we found 155 ppb under $P_{HCl}=1.67\times10^{-3}$ Pa. If we compare their results to ours according to Eq. (1), i.e. assuming that kinetic processes rule incorporation, then their concentration is a factor of 2.3 lower than expected from our results. On the other hand, if the comparison is done using Eq. (2), i.e. using a $P_{HCl}^{\frac{1}{2.73}}$ dependence, then their result should be 1.5 times greater than ours, i.e. 232 ppb, definitely within the overlap of their error bars and ours. Since Diehl et al. used a set up very different from ours that could result in a different value of h, and since according to Eq. (3) the value of h greatly influences X_{HCl}, we conclude that the X_{HCl} value of Diehl et al. is compatible with ours. However, their purpose was not to test the impact of the growth rate on HCl incorporation, and their data can thus not be used to test our mechanism.

The variability of crystal growth parameters such as h, but also α_{H2O} and α_{HCl}, with experimental conditions thus makes it difficult to intercompare experiments. The application of laboratory data to natural conditions is even more delicate and deserves a separate discussion.

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4. Application to snowpacks and clouds

The main conclusion of this work is that the experimental data obtained is consistent with the mechanism of Domine and Thibert (1996), which showed that the composition of ice depends on its growth rate and on the details of its growth mechanism. Given that we have argued that the variables that determine the growth of snow crystals, and hence the incorporation of trace gases, vary between different laboratory experiments, and presumably between the different conditions encountered in clouds and in snowpacks, quantitative application of this mechanism to the natural environment appears impossible until we understand the details of ice crystal growth in nature, and we seem to be very far from this goal. Domine et al. (2003) may have observed growth steps on surface hoar crystals studied by scanning electron microscopy (SEM), and whose height was about 1 μm, but it is not even totally certain that the structures observed were growth steps, and they did not seem to originate from a crystal edge, but rather from a grain boundary, so that the representativity of this observation may be limited. Indeed, the numerous SEM studies of snow crystals (Wergin et al., 1996; Domine et al., 2003; Erbe et al., 2003; Legagneux et al., 2003) usually do not show any structures that can be convincingly attributed to growth steps, which suggest that these could be undetectable by SEM and much smaller than 1 μm in most cases.

Furthermore, in nature, the ice surface and the adsorption of trace gases can be modified by the presence of numerous pollutants. For example Hynes et al. (2002) have observed that adsorbed HCl was displaced from the ice surface in the presence of HNO_3. The ubiquitous sulphate aerosols can also be scavenged by ice surfaces and form a liquid or disordered film that could dramatically modify ice surfaces and the incorporation of trace gases, as the first step in incorporation is adsorption.

Given our limited understanding of the growth of snow crystals in nature, we are limited to speculate qualitatively on the interactions between crystal growth rate and chemical composition. For species highly soluble in ice such as HCl, $X_{kin}<X_{eq}$ under most atmospheric conditions and faster growth rates will lead to lower concentrations.

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Thus, the small columnar ice crystals that form slowly in cirrus clouds at low temperature should be more concentrated in Cl^- that the larger dendritic crystals that grow rapidly in the warmer stratiform clouds. In the snowpack, the rapidly growing depth hoar crystals should be depleted in Cl^- relative to windpack crystals, that grow much more slowly. This should be true at least in acidic snow, where the Cl^- measured by ion chromatography indeed reflects HCl content, while it would have little reason to hold in alkaline snow, where the Cl^- signal reflects the content of particulate Cl^-, present in snow as a salt such as NaCl. Field measurements of different snow crystal types in a given snow pack would be a reasonably easy test of this prediction.

The situation is probably different for HNO_3, which is about 20 times less soluble in ice than HCl (Thibert and Domine, 1998). In this case, the data available suggest that at high temperature, we still have $X_{kin}<X_{eq}$, but at low temperature, we should have $X_{kin}>X_{eq}$. The limit between "high" and "low" temperature will depend on the physics of ice crystal growth, and particularly on *h*. In the Arctic or subarctic snowpack, since depth hoar crystals are at the relatively warm bottom part of the snowpack while windpacks are at the colder top part (Domine et al., 2002), we have all reasons to expect a higher NO_3^- concentration in the windpack, and again this prediction only applies to acidic snow.

5. Conclusions

The experiments performed here are consistent with the predictions of the mechanism of Domine and Thibert (1996) that proposed an interaction between the growth rate of ice crystals and their chemical composition. The nature of the crystallographic face, the nucleation mechanism and step height, *h*, of new ice layers, and other variables describing the state of the growing ice surface will influence ice composition. The immediate implication is that considerable efforts must be devoted to the physics of ice crystal growth under natural conditions if we want to understand the composition of ice crystals in clouds and in the snowpack.

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It is also noteworthy that this mechanism does not need to invoke the much talked about "quasi-liquid layer" (QLL) on the ice surface. It is certain that this QLL does exist, as it has been evidenced by numerous techniques (Petrenko and Witworth, 1999), including a recent study by atomic force microscopy (Döppenschmidt and Butt, 2000) that concluded that its thickness at −15°C was between 5 and 10 nm. Several authors (e.g. Valdez et al., 1989; Conklin and Bales, 1993) have interpreted gas uptake by growing ice in terms of solubilization of the gas in the QLL, using thermodynamic parameters of actual liquid water. But the QLL properties are definitely different from those of liquid water, and using parameters measured for liquid water is unwarranted. Moreover, the model used by those authors led them to conclude that the QLL thickness in pure ice was greater than 100 nm at −15°C, in sharp contrast with the actual measurements of Döppenschmidt and Butt (2000). Further supporting the idea that the QLL need not be invoked to explain ice growth at −15°C, many physical properties of ice growth have been explained successfully by considering solid state processes only (Libbrecht, 2003a, b; Nelson and Baker, 2003; Nelson, 1998; Nelson and Knight, 1998).

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Table 1. Experimental conditions and results for the incorporation of HCl in ice as a function of the supersaturation of the gas mixture in H_2O relative to ice at −15°C.

Experiment duration (h)	Supersaturation (%)	P_{HCl} (Pa)	Number of experiments	Average $[Cl^-]$ (blank subtracted) (ppb molar)	Standard deviation (ppb molar)
64	15	1.67×10^{-3}	4	155	48
26	40	1.67×10^{-3}	1	24	–
16	82.5	1.67×10^{-3}	5	11	7

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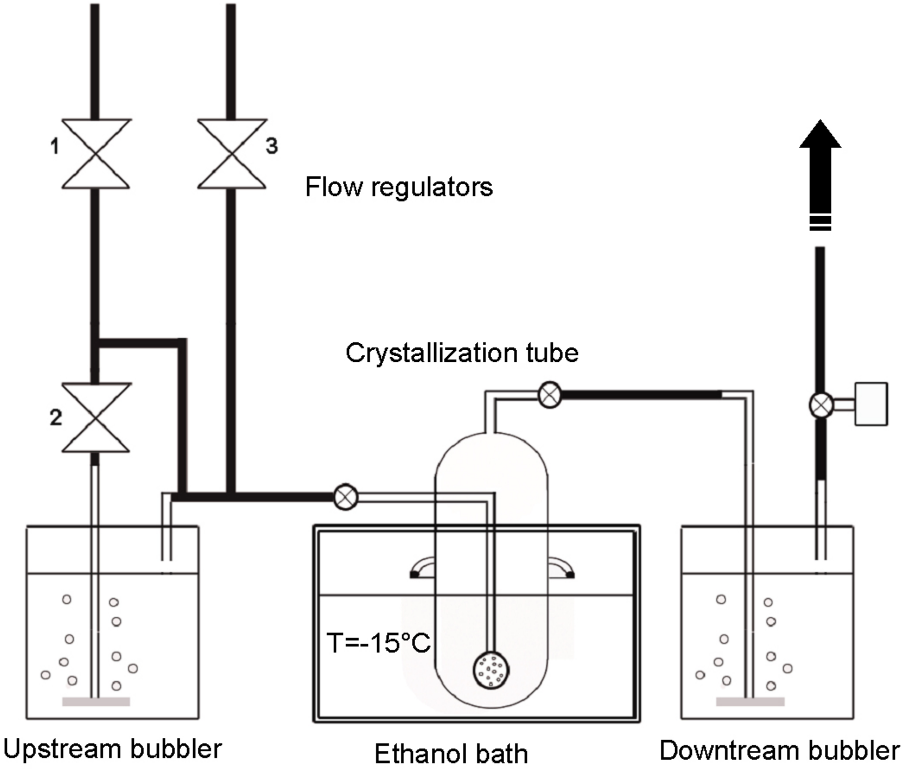

Fig. 1. Experimental system used to study the incorporation of HCl in growing ice crystals. Three flow regulators and a bubbler filled with ultra pure water are used to set the partial pressures of HCl and H_2O diluted in N_2 at atmospheric pressure. The crystallization tube is partly immersed in an ethanol bath at −15°C. A second bubbler is sometimes added downstream of the cold bath to trap HCl.

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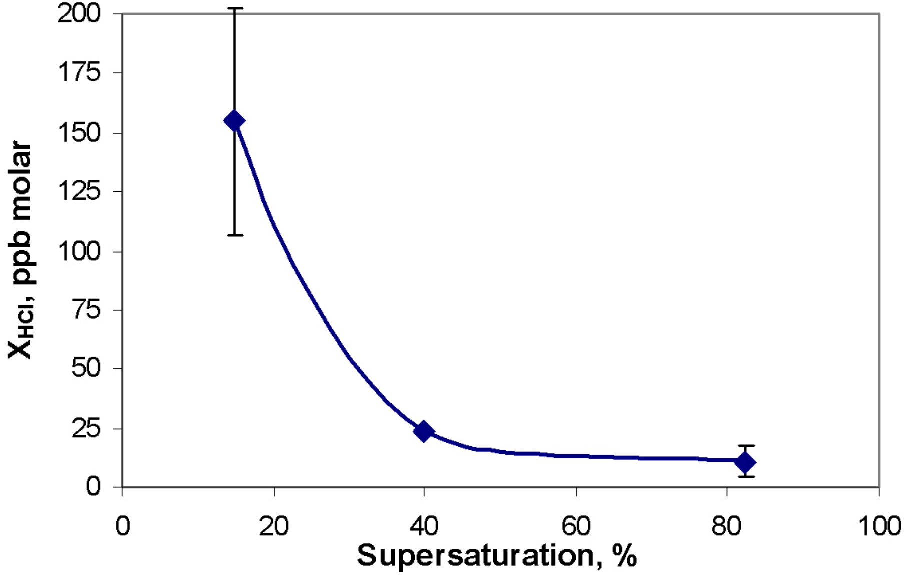

Fig. 2. Molar fraction of HCl (detected as Cl^- by ion chromatography) in ice as a function of the supersaturation of the gas mixture relative to ice at −15°C. Error bars are the standard deviations when several experiments were made (see Table 1). The line is a visual aid.

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