NO Adsorption on Ice at Low Concentrations

RICHARD A. SOMMERFELD,*,[1] MARTHA H. CONKLIN,† AND S. KAY LAIRD*

*U.S.D.A. Forest Service, 240 West Prospect Road, Fort Collins, Colorado 80526; and †Department of Hydrology and Water Resources, Geology Building 11, University of Arizona, Tucson, Arizona 85721

Received June 20, 1991; accepted September 17, 1991

To better understand the properties of ice surfaces at different temperatures, the adsorption of a relatively insoluble gas, NO, was studied using a continuous-flow column experiment. Adsorption isotherms for NO on the surface of ice were measured for a temperature range of −1 to −70°C and a concentration range of 10 to 250 ppbv. Very little adsorption was measured; surface concentrations were near the detection limit of $\pm 10^{-10}$ g m^{-2}, limiting the precision of the data. Although a relatively large proportion of ice–ice surfaces were present, no grain boundary effect was detectable. NO sorption was observed to increase with decreasing temperature. From a van't Hoff plot, preliminary evidence indicating a change of sorption mechanism at −10°C was obtained. This may be evidence for the effects of surface premelting.

INTRODUCTION

The adsorption of gases on the surface of ice at temperatures near the melting point is of interest to provide basic data on pollutant interactions with ice and to elucidate the chemical nature of the ice surface. Airborne pollutants can interact with ice surfaces in the atmosphere and on the ground (1–4). The nature of these interactions may be complicated by surface premelting of the ice at earth surface temperatures, which are normally within 90% of the melting point (5–9). However, there is little agreement in the literature on the nominal thickness or temperature range of existence of what has been termed a quasi-liquid layer (6, 10).

The effect of the quasi-liquid layer has been observed previously (2, 11–13). These studies showed increases of adsorption with increasing temperature in the temperature range −35 to 0°C for a variety of chemical species. This adsorption behavior is anomalous to that of most gases adsorbed on solid surfaces and has been attributed to the thickening of the absorbing surface layer at higher temperatures. This may be evidence of surface premelting (14). In addition to surface premelting effects, there is evidence that chemical species may migrate along ice–ice grain boundaries (6, 13, 15, 16).

Sorption and desorption processes on ice surfaces will involve dissolution of NO when the quasi-liquid layer is present and physical adsorption at temperatures where it does not exist. If equilibrium partitioning between the gas and solid phase is assumed, the following governing equations can be used to describe one-dimensional solute transport of a dilute mixture of NO passing through a column packed with ice spheres,

$$\phi \frac{\partial S}{\partial t} + \theta \frac{\partial C}{\partial t} = \theta D_a \frac{\partial^2 C}{\partial z^2} - v\theta \frac{\partial C}{\partial z} \quad [1]$$

$$S = KC, \quad [2]$$

where C is the gas phase concentration (μg cm^{-3}), S is the sorbed concentration (μg g^{-1}), θ is the void fraction of the column, ϕ is the dry bulk density of the ice, D is the longitudinal dispersion coefficient (cm^2 s^{-1}), K is a partition coefficient (cm^3 g^{-1}), and v is the inter-

[1] To whom correspondence should be addressed.

0021-9797/92 $3.00

stitial velocity (cm s^{-1}). Analytical solutions have been presented elsewhere (17–19).

At different temperatures, K will represent partitioning either between the gas phase and the premelt surface layers (at higher temperatures) or between the gas phase and the ice surfaces at lower temperatures.

The retention volume of NO in the experimental apparatus (V_a) can be partitioned as

$$V_a = V_{pa} + V_s + V_{ri}, \qquad [3]$$

where V_{pa} is the parasitic retention of the apparatus consisting of the apparatus dead volume and the volume retained by adsorption on the apparatus walls. V_s is the sample void volume and V_{ri} is the volume retained by adsorption on the ice,

$$V_{ri} = V^0_{ri} A_{si}, \qquad [4]$$

where V^0_{ri} is the specific retention volume, per surface area, and A_{si} is the ice surface area. We varied A_{si} by approximately a factor of 5 by using 250- and 50-mm-length sample tubes in separate experiments. This resulted in two equations in two unknowns which could then be solved for V^0_{ri} and V_{pa}.

MATERIALS AND METHODS

We used the frontal development technique of gas chromatography (2, 13, 20). A flow of carrier gas through the pair of ice-packed columns was established, the test gas (NO) was injected into the carrier at the upstream end of the test column, and the breakthrough curve was measured until it reached the concentration of the input gas.

A block diagram of the apparatus is shown in Fig. 1. A feature of the apparatus is the conditioning tube in which the carrier gas (artificial air) is humidified and temperature equilibrated before it enters the test column (21). In these experiments, test columns of 50 and 250 mm length were used. Besides the ice, the gas contacted primarily Teflon and small amounts of 316 stainless steel surfaces. The cold chamber was a Despatch Model 900 environmental chamber which controlled the temperature to better than ±0.2°C.

The columns were packed with ice spheres

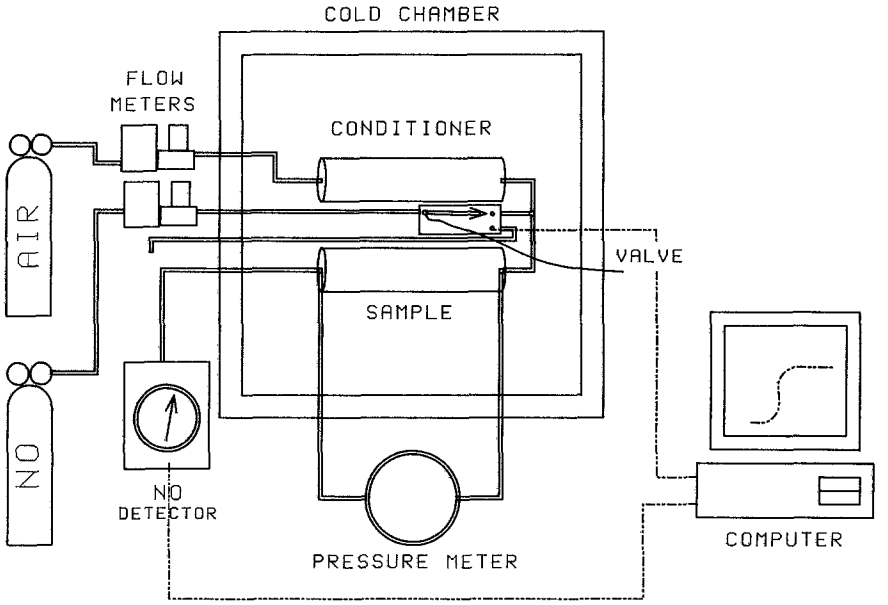

FIG. 1. Schematic of the apparatus.

of about 100 μm in radius (22). Spheres of this size have a specific surface energy sufficiently low that the rate of change of size is very low (23). The Pyrex columns were 12.5 mm in radius, and their interior surfaces were coated with a thin layer of ice to eliminate adsorption of gases on the glass and to ensure that the ice spheres adhered to the walls of the column. The packed columns were allowed to sinter for more than 5 days at about −25°C to eliminate the smallest radii, especially at the contacts between spheres. The ice surface area in columns prepared in this way was stable for the course of the experiments. The packed columns actually consisted of a collection of different crystal faces (but not necessarily facets). Differences in adsorption on the different faces may be significant but measurement would require a different technique. Mitra *et al.* (24) did not show any significant differences between their SO_2 adsorption measurements on vapor-grown ice crystals and the adsorption of SO_2 on ice spheres measured by Sommerfeld and Lamb (2) and Clapsaddle and Lamb (13). This indicates that adsorption on different crystallographic faces may not be sufficiently different to be detected by these techniques.

The void volumes in the columns were measured by weighing the packed tubes. We determined the role of the ice surfaces by comparing the results of measurements with two different column lengths: 250 and 50 mm. Since the other apparatus void volume and adsorbing surfaces remained the same, we could determine the effect of the ice itself by difference, as discussed above. The apparatus void volume was about 450 mm^3, about 2% of the test column void volume.

The specific surface area was measured with a stereological technique as described by Perla *et al.* (25). Samples were cut from each end and the center of each column for these measurements. The void space in these samples was also determined stereologically. The consistency of the void space determined this way within each column and with the void space determined by weight (±10%) showed that the columns were uniformly packed. Although they are difficult to detect, isolated voids were never seen while making the surface sections or analyzing the resulting photographs. The preparation of the samples from ice spheres and their high porosities (>0.35) would not lead to a significant concentration of isolated voids.

The specific ice–ice grain boundary area was determined using the stereological technique. In this case, the traces of the boundaries on the surface section were measured by hand for one specimen, which was assumed to be representative. No ice–ice grain boundary effect was detected (see below) so only limited measurements of the ice–ice grain boundary concentration were performed.

NO was Air Products-analyzed 9-ppm nitric oxide in nitrogen. Flows were controlled by Matheson Model 8209 mass flow controllers with a nominal accuracy of 1%. Periodic calibration with a bubble flow meter confirmed that the controllers operated to at least this accuracy. Different concentrations were obtained by varying the different flows. The total flow was kept constant at 300 SCCM, somewhat above the requirements of the detector.

The NO detector was a Monitor Labs Model 8840. Its time constant was set to 5 s. The actual response was measured by valving different concentrations of NO directly into its intake. The output from this approximate square wave input was fitted to an exponential function of the form $(1 - e^{-t/\tau})$ to determine the time constant, τ. Experimental curves were corrected using the above function before any other analysis.

The valving and data acquisition were controlled with an AT&T 6300 computer using a Data Translation DT2801 interface card. A program was written in ASYST to run the experiments. Time was measured every 0.1 s to an accuracy of 1 ms. Flow times for the test gas in a preliminary set of experiments were determined from the midpoints of the breakthrough curves. Retardations for the final experiments were determined by fitting the data to a two-parameter, equilibrium model using

a program developed by Parker and van Genuchten (19).

RESULTS

Adsorption quantities for the preliminary experiments with the 50-mm tubes corrected for the void volume are shown in Fig. 2. A slight trend of increased adsorption is evident from the warmer to the colder temperatures; however, the trend is about the same magnitude as the scatter in the data. The main conclusion is that the adsorption in the ice is less than the scatter among the different measurements. If adsorption in the ice were detectable in this set of experiments, the data would exhibit a variation with temperature similar to but of a smaller magnitude than that of the 250-mm tubes.

Figure 3 shows the adsorption for the preliminary experiments with the 250-mm tubes corrected for the void volume. For calculations, the data points were fitted to simple power functions to smooth the data. The limited precision of the data is indicated by the scatter of the points around the fitted curves and the fact that the isotherm for −10°C lies below that for −3 and −5°C and the isotherm for −30°C lies below that for −20°C, the reverse of normal adsorption. While the slight curvature in fitted curves appears to be reproducible, the curves are very close to linear.

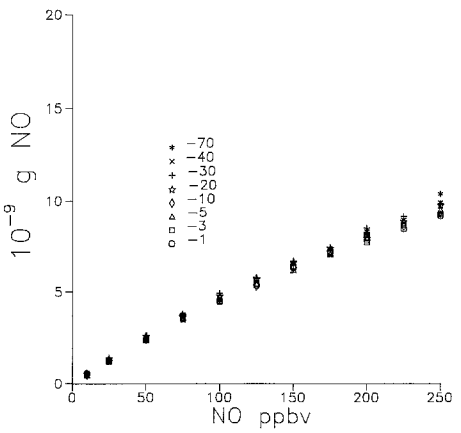

FIG. 2. NO adsorption isotherms; 50-mm tube.

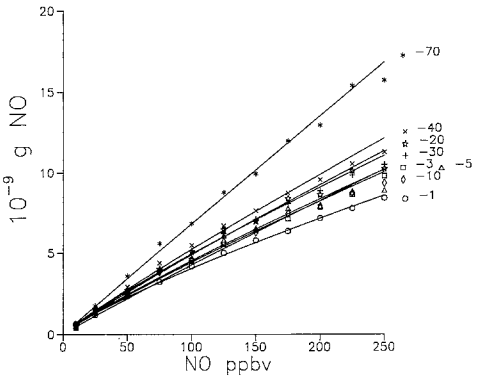

FIG. 3. NO adsorption isotherms; 250-mm tube.

A comparison between these data indicates that adsorption on the ice (V_{ri}) is a small percentage of the total adsorption in the apparatus (V_a). The wall loss to the apparatus might be due to NO reacting with impurities in the stainless steel (26). Thus, minor variations in the apparatus adsorption and in the flow rates on the different days when the experiments were performed could cause enough experimental error to obscure the data. For that reason, a second set of experiments was performed at 250 ppbv and −3, −10 and −40°C in which 50-mm and the 250-mm tubes were compared on the same day; 250 ppbv was chosen because the precision of the measurements is greater at higher concentrations and the preliminary experiments showed that the variation of adsorption with concentration is essentially linear below 250 ppbv.

Figure 4 shows the results of the second set of experiments and the −70°C data derived from the preliminary experiments. The −3°C value is the result of a single run. The −10°C value is the result of two 50-mm and one 250-mm runs, while the −40°C is the result of two 250-mm and one 50-mm run.

Total retention volumes (V_a) and the resulting ice retention volumes (V_{ri}) for the second set of experiments are given in Table 1. The scatter in retention volumes for the same specimen on the same day is a little larger than 1%, consistent with the accuracy of the flow controllers. The ice adsorption volumes for the

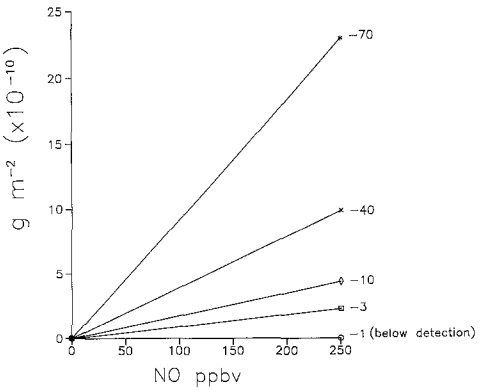

FIG. 4. Adsorption isotherms of NO on ice at different temperatures; 250-ppbv data.

250-mm tubes are roughly 2% of the total retention volume. From these comparisons, we conclude that the accuracy of the adsorption determinations in the second set of experiments is about ±50% and that the adsorption at −1°C is at the limit of detectability, which is about 10^{-10} g m^{-2}.

Figure 5 shows a van't Hoff plot of the points at 250 ppbv. Zero is taken as the limit of accuracy of the data, 10^{-10} g m^{-2}. ΔH for the adsorption between −10 and −70°C is 2.6 kcal mol^{-1}. Above −10°C, the apparent ΔH is a much larger positive value. It is also obvious that the assumption that ΔH is independent of temperature is not good in the region −1 to −10°C. The data are consistent with the hypothesis that the sorption in this range represents solution in a quasiliquid layer whose thickness increases with increasing temperature. We interpret the change of slope as indicating a change of adsorption mechanism or anomalous adsorption associated with surface premelting. This result is consistent with measurements for a number of other compounds (2, 11–13).

The ratio of ice–air surface to ice–ice surface was about 3:1 in the single sample measured. If grain boundary adsorption were important, this amount of ice–ice surface would certainly be significant. However, the adsorption and desorption were complete in less than 20 s, indicating that for NO there was little diffusion into grain boundaries even at temperatures where surface premelting is likely to enhance grain boundary transport. This contrasts with the results of Clappsaddle and Lamb (13) on SO_2 adsorption on ice. They found two equilibrium adsorption mechanisms, one with a relatively short adsorption time and one with a much longer time. Their results might be explained by a grain boundary effect.

SUMMARY

It is evident that NO is a conservative species regarding adsorption on ice. Even at −70°C the quantity adsorbed is negligible as far as atmospheric or snowpack processes are concerned. There is evidence of anomalous adsorption near the melting point, consistent with adsorption measurements with other compounds. We attribute the change in mechanism to the existence of a surface pre-

TABLE I

Temperature (°C)	Column length (mm)	Apparatus retention volume V_a (cc)	Ice retention volume V_{ri} (cc)	Average V_{ri}	Surface concentration (×10^{-10} g m^{-2})
−3	50	56.3	—		
	250	96.0	1.6	1.6	2.3
−10	50	62.0	2.7		
	50	61.5	3.3	3.0	3.0
	250	102.6	—		
−40	50	58.7	—		
	250	103.5	7.9		
	250	101.9	5.8	6.8	9.8

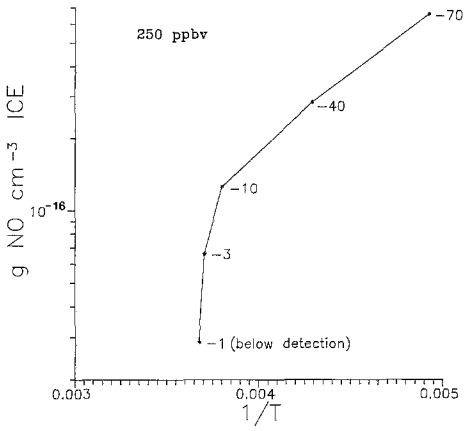

FIG. 5. van't Hoff-type plot of the 250-ppbv isotherms.

melting layer at temperatures above −10°C and its disappearance below −40°C. The sorption mechanism at the warmer temperatures would be partitioning into the surface premelting layer while physical adsorption would dominate at the colder temperatures. There is no evidence of diffusion into the ice–ice grain boundaries, although a significant number of such boundaries were present in the sample. This is not surprising considering the very low adsorption observed at temperatures where surface premelting might aid such diffusion (6).

REFERENCES

1. Sommerfeld, R. A., *in* Acid Deposition in "Colorado—A Potential or Current Problem; Local versus Long-Distance Transport into the State" (R. A. Pilke, Ed.) CIRA, Fort Collins, CO 1986.
2. Sommerfeld, R. A., and Lamb, D., *Geophys. Res. Lett.* **13,** 349 (1986).
3. Molina, M. J., Tso, T. L., Molina, L. T., and Wang, F. C., *Science* **238,** 1253 (1987).
4. Wofsy, S. C., Molina, M. J., Salawitch, R. J., Fox, L. E., and McElroy, M. B., *J. Geophys. Res.* **95,** 2442 (1988).
5. Fletcher, N. H., "The Chemical Physics of Ice." Cambridge Univ. Press, Cambridge, England, 1970.
6. Hobbs, P. V., "Ice Physics." Oxford Univ. Press, London, 1974.
7. Valdez, M. P., Bales, R. C., Stanley, D. A., and Dawson, G. A., *J. Geophys. Res.* **92,** 9700 (1986).
8. Furukawa, Y., Yamamoto, M., and Kuroda, T., *J. Cryst. Growth* **82,** 665 (1987).
9. Mizuno, Y., and Hanafusa, N., *J. Phys. C* **48**(1), 511 (1987).
10. Golecki, I., and Jaccard, C., *J. Phys. Solid State Phys.* **11** (1978).
11. Adamson, A. W., "Physical Chemistry of Surfaces." Interscience, New York, 1982.
12. Ocampo, J., and Klinger, J., *J. Phys. Chem.* **87,** 4167 (1983).
13. Clapsaddle, C., and Lamb, D., *Geophys. Res. Lett.* **16,** 1173 (1989).
14. Nenow, D., *Prog. Cryst. Growth Charact.* **39,** 185 (1984).
15. Mulvaney, R., Wolff, E. W., and Oates, K., *Nature* **331,** 247 (1988).
16. Wolff, E. W., Mulvaney, R., and Oates, K., *Geophys. Res. Lett.* **16,** 487 (1989).
17. Lapidas, L., and Amundson, N. K., *J. Phys. Chem.* **56,** 984 (1952).
18. Lindstrom, F. T., Hague, R., Freed, V. H., and Boersma, L., *Environ. Sci. Technol.* **1,** 565 (1967).
19. Parker, J. C., and van Genuchten, M. Th., "Virginia Agricultural Experiment Station," Bulletin 84-3, 1984.
20. Purnell, H., "Gas Chromatography." Wiley, New York, 1962.
21. Arancibia, E. L., and Catoggio, J. A., *J. Chromatogr.* **197,** 135 (1980).
22. Sommerfeld, R. A., and Freeman, T. L., Research Note RM-486, USDA Forest Service, Rocky Mountain Forest and Range Experiment Station, Fort Collins, 1988.
23. Perla, R., *in* "Comptes rendus. Deuxieme Recontre Internationale sur la Neige et les Avalanches, Avril 12–13," p. 43. Grenoble, France, 1978.
24. Mitra, S. K., Barth, S., and Pruppacher, H. R., *Atmos. Environ.* **24A,** 2307 (1990).
25. Perla, R. I., Dozier, J., and Davis, R. E., *J. Micros.* **141,** 111 (1986).
26. Hilliard, J. C., and Wheeler, R. W., *Combust. Flame* **29,** 15 (1977).